THE APPLICATION OF LIQUID EXTRACTION TO THE REMOVAL OF ORGANIC CONTAMINANTS FROM WATER

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The Application of Liquid Extraction to the Removal of Organic Contaminants from Water

by

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Summary

In this report, the feasibility is examined of using liquid extraction for the removal of organic compounds from water which has been contaminated by a chemical spill or by a leaking chemical landfill.

Equilibrium partition coefficients (K_{sw}) were measured and are reported for six solutes: acetone, 1,2-dichlorobenzene, 1,2-dichloroethane, ethylbenzene, 1,1,2,2-tetrachloroethane and toluene, between water and five solvents: dichloromethane, ethylbenzene, Isopar M, octane and octanol. A high value for the K_{sw} indicates that the solvent will effectively remove the solute from the water. A novel method for the measurement of K_{sw} involving sequential extractions of the solute from the solvent by water was developed. The technique is particularly suitable for systems which have a K_{sw} value greater than 100. The selection of a solvent for a particular application will also depend on other properties such as toxicity, stability, cost and availability.

Isopar M, a low aromatic-content kerosene, was selected as the most suitable solvent and was used in a pilot scale continuous countercurrent reciprocating plate extraction column to remove the candidate solutes, toluene and 1,1,2,2-tetrachloroethane from water. Removal efficiencies of 99% for toluene and 85% for 1,1,2,2-tetrachloroethane were obtained using a solvent to water volumetric flow ratio of 1:20. Preferred operating conditions are described. The feasibility of solvent recovery by steam stripping the solutes from the solvent is investigated theoretically and by experiment.

It is concluded that liquid extraction is feasible as a method of removing hydrophobic organic compounds from water. The solvent can be recovered by steam stripping provided that the vapour pressures of the solute and solvent are sufficiently different. A full scale design of a mobile unit with a capacity of 3.0 m^3/h of contaminated water is presented and costed. Recommendations are made for further study including tests to determine whether the solvent can be recycled without a loss of efficiency.

Resumé

Dans le présent rapport, on examine la faisabilité de l'extraction liquide pour l'élimination de composés organiques dans de l'eau contaminée par un déversement accidental de produits chimiques ou par des fuites provenant d'une décharge qui en renferme.

Les coefficients de partage à l'équilibre (K_{SE}) ont été mesurés et sont donnés pour six solutés, à savoir l'acétone, le 1,2-dichlorobenzène, le 1,2-dichloroéthane, l'éthylbenzène, le 1,1,2,2-tétrachloroéthane et la toluène entre l'eau et cing solvants, le dichlorométhane, l'éthylbenzène, l'Isopar M, l'octane et l'octanol. Une valeur élevée pour K_{SE} montre que le solvants séparera efficacement le soluté de l'eau. On a mis au point une nouvelle méthode pour la mesure de K_{SE}, consistant à partir de solvant. La technique convient particulièrement bien pour des systèmes dont le K_{SE} est supérieur à 100. Le choix d'un solvant pour une application particulière est également fonction de facteurs comme la toxicité, le coût et la possibilité de se procurer le produit.

Isopar M, un kérosène à faible teneur aromatique, a été choisi, à l'échelle pilote, comme solvant le plus approprié dans une colonne d'extraction à plateaux oscillants, fonctionnant à contre-courant et en continu, pour éliminer les solutés, soit le toluène et le 1,1,2,2-tétrachloroéthane, dans l'eau. On a obtenu des taux d'élimination de 99% pour le toluène et de 85% pour le 1,1,2,2-tétrachloroéthane avec un rapport de débits volumétriques solvant/eau de 1/20. Le mode opératoire choisi est décrit. La possibilité de récupérer le solvant par extraction à la vapeur des solutés qu'il renferme est examinée théoriquement et expériemtnalement.

On en arrive à la conclusion que l'extraction liquide est une méthode valable pour extraire de l'eau les composés organiques hydrophobes. Le solvant peut être récupéré après purification à la vapeur, à condition que les pressions de vapeur du soluté et du solvant soient suffisamment différentes. On présente une unité mobile à l'échelle réelle, dont la capacité est de 3.0 m3/h d'eau contaminée, et on en évalue le coût . D'autres études sont proposées, notamment des essais pour déterminer si le solvant peut être recyclé sans perte de rendement ultérieur.

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1. Introduction

The need for improved chemical spill cleanup technology has been brought to the forefront of public concern recently with the increased realization of the negative effects of chemicals in the environment. Canada's extensive networks of lakes and rivers are frequently contaminated by spills, and groundwater is affected by spills on soil or by leaking chemical landfills. The Canadian landscape and climate present challenges in planning spill countermeasures. Emergency response teams must not only be prepared for spills in city centres but in remote areas as well. The equipment must be adaptable for winter and summer conditions, with operating temperatures ranging from -30°C to 30°C.

Environment Canada is currently developing several chemical treatment processes capable of dealing with the wide range of spilled chemicals encountered in Canada. This involves extensive research into adapting existing technologies and developing new technologies for water treatment. The goal is to construct a process train consisting of a series of unit operations which can be transported to a spill location for on-site treatment. Depending on the chemical, it may be recovered in concentrated form or it may be destroyed. One existing technology which is adaptable to water treatment and is the subject of this study is liquid extraction.

Liquid extraction (LE) has been used extensively throughout various industries. In the mining and metal industries extraction is used to separate metals and to recover inorganic chemicals from solutions and slurries. The nuclear industry uses solvent extraction to recover uranium from process liquors and also to refine the uranium oxide fuel (Flett, Melling and Cox, 1983). In oil refining and coal and coke processing, LE is used to remove phenol from waste water (Earhart et al., 1974, Gravelle and Panayiotou, 1980, Greminger et al., 1982, Mackay and Medir, 1983, Medir et al., 1985). The petrochemical industry separates aliphatic and aromatic components in the purification of kerosene and lube oil by extraction and isolates the benzene, toluene and xylene fractions for the production of nylon, styrene and terylene (Bailes, 1983). LE is also used in the manufacture of antibiotics such as penicillin (Ridgeway and Thorpe, 1983), in the decaffination process as well as for the extraction of flavours and aromas (Hamm, 1983).

Despite its diverse applications, LE has not generally been used to remove pollutants from aqueous effluents. The principal reason is that unless a solute is valuable, the expense of liquid extraction and solvent (and solute) recovery cannot be justified. Therefore, LE is used to remove and recover a single compound from a process stream either because of its economic worth or because it creates problems for the downstream process. Recently, however, LE has been considered for treatment of a water stream containing a wide range of contaminants (King et al., 1984). It has been suggested that kerosene would be a satisfactory solvent for extracting a range of organic contaminants from water.

The aim of this study is to demonstrate the feasibility of LE for the purification of water contaminated with organic chemicals as may be encountered under environmental emergency conditions. Accordingly, the partitioning of six organic solutes between water and four different solvents is investigated. The results are analysed for trends attributable to the different physical and chemical properties of the solutes and solvents. The partition coefficents determined by experiment are compared with literature values of similar systems.

In a second study, a pilot scale extraction column is used on two test chemicals to show the validity of the lab scale measurements and to obtain data for a full scale design. The full scale design includes a liquid extraction column and provision for solvent recovery in a mobile process train of unit operations. The cost of the mobile unit is estimated.

Conclusions regarding the feasibility of LE for this application are reached and recommendations for future study are made.

2. Literature Review

2.1 Introduction

A typical liquid extraction system for the treatment of contaminated water involves three components: an extraction process, a solvent removal process and a solute removal process (Figure 2.1) During the extraction process, the feed stream is contacted by the solvent to remove the solute from the water. The exiting water, called the raffinate, is saturated with the solvent and depending on the solvent's solubility in water and its toxicity may require further processing to remove the solvent. The extract, i.e. the solute-laden solvent, must be treated to recover both the solvent (for recycle) and the solute. Without this recovery step, LE would not be economical. Variations to the flow configuration can be made for systems using a dual-solvent mixture (Earhart et al., 1977, Gravelle and Panayiotou, 1980, Kiezyk and Mackay, 1971).

2.2 General Principles of Solvent Selection

The choice of a particular solvent for the removal of a compound from water requires a balance between the selectivity and the capacity of the solvent for the solute (Hampe, 1986 and Munson and King, 1984). Selectivity is a measure of the preference a solute shows for one phase over the other. A high selectivity for the extracting solvent is important when two solutes require separation from a solvent. The extractant preferentially removes one solute, leaving the other behind.

When considering the extraction of a range of contaminants from a water stream, the capacity of the solvent is also of concern. The ideal solvent should be selective for the solute (in preference to water) and it should have the capacity to dissolve a large quantity of solute, i.e. the solubility of the solute in the solvent should be large. Partitioning is defined by the equilibrium partition coefficient of the solute, K_{ow}:

$$K_{ow} = C_o/C_w \qquad [2\text{-}1]$$

where,

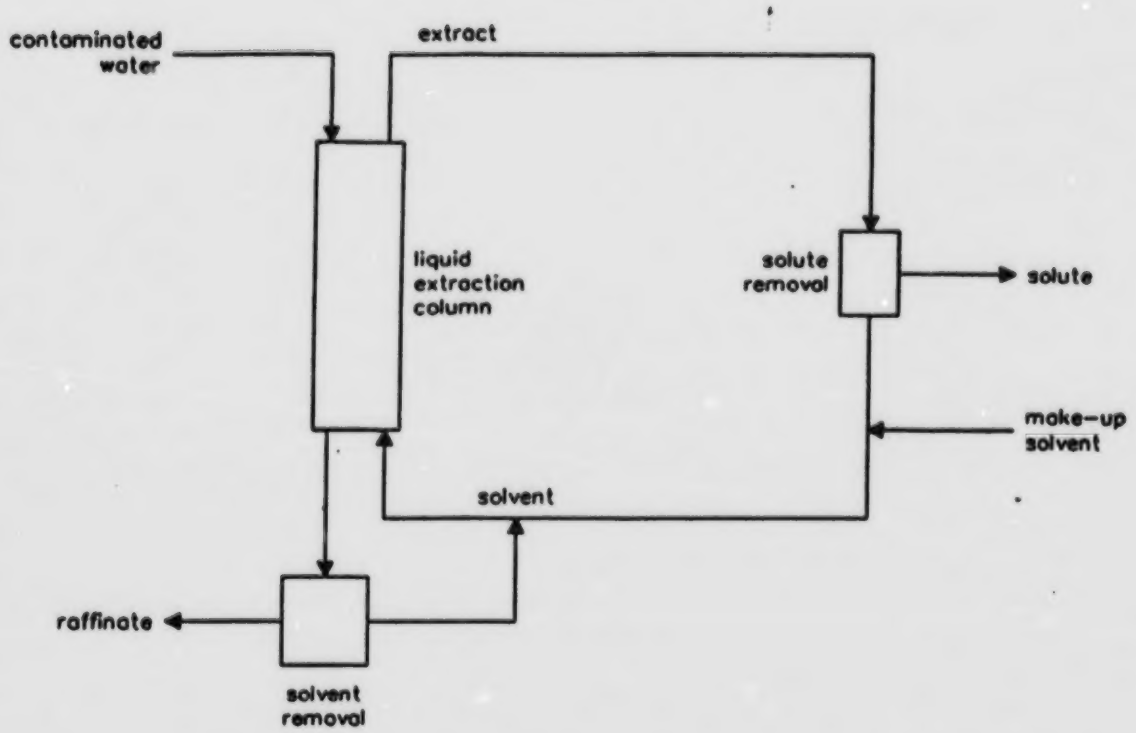


Figure 2.1 Schematic of a Typical Liquid Extraction Process

C_i is the concentration of solute in phase i (g/m^3), and the subscripts s and w denote the solvent and water phases. The partition coefficient can also be expressed thermodynamically, based on fugacity, f, or activity, a. At equilibrium,

$$f_s = f_w \text{ or } a_s = a_w \qquad [2\text{-}2]$$

from which,

$$x_s\gamma_s = x_w\gamma_w \qquad [2\text{-}3]$$

where,

x_i is the mole fraction of the solute in phase i, and γ_i is the activity coefficient of the solute in the indicated phase. If the partition coefficient is defined on a molar basis,

$$k_{sw} = x_s/x_w = \gamma_w/\gamma_s \qquad [2\text{-}4]$$

The thermodynamic partition coefficient, k_{sw}, is related to K_{sw} as defined in [2-1] by,

$$K_{sw} = C_s/C_w = (x_s/v_s)/(x_w/v_w) = k_{sw}(v_s/v_w) \qquad [2\text{-}5]$$

where,

v_i is the molar volume in phase i. A high partition coefficient implies that a low solvent to water flow ratio is possible.

Mixtures of two solvents, usually one polar solvent and one volatile solvent have been shown to be more effective than either of the two solvents alone (Earhart et al. 1974, 1977, Gravelle and Panayiotou, 1980, Hwang, 1982, Mackay and Medir, 1983, and Medir et al., 1985). Unfortunately, selection of the two solvents and the optimal mixture composition must be determined experimentally (Munson and King, 1984). The use of mixed solvents may make the solvent recovery process more complex.

2.3 Measurement of the Partition Coefficient

The most common method of measuring equilibrium partition coefficients is to determine the concentration of the solute in each phase, either directly or by difference, and to calculate K_{sw} by equation [2-1]. When K_{sw} is very large (ie. 300 or more), as applies for most of the systems of concern in this study, the equilibrium concentration in the water phase is very low. Extraction of the water phase by another solvent is often necessary to concentrate the sample so that the amount of solute is quantifiable. Each treatment step in the analytical process introduces a source of error, thus reducing the accuracy in the values obtained. However, unless the absolute amount of solute

determined by GC analysis is determined with an accuracy of 2-3% of the amount of solute added to the samples, the accurate determination of the water phase concentration is critical to K_{ow} measurement. In response to these difficulties, a second method for partition coefficient measurement was developed in this study and is described here. It is termed the "sequential extraction" technique.

A large volume of water is used to sequentially extract the solute from a small volume of "spiked" solvent. The solvent is analysed to determine the change in solute concentration after each extraction. The water concentrations are not measured. The concentration in the solvent after the first extraction, C_1, is related to the feed concentration, C_o, by:

$$C_1 = C_o/(1+V_w/V_s.K_{ow}) \qquad [2\text{-}6]$$

and after the n^{th} extraction,

$$C_n = C_o/(1+V_w/V_s.K_{ow})^n \qquad [2\text{-}7]$$

by taking the logarithm of both sides and rearranging, [2-7] becomes:

$$\log (C_n/C_o) = -n\log (1+V_w/V_s.K_{ow}) \qquad [2\text{-}8]$$

A plot of $\log(C_n/C_o)$ versus the extraction number, n, yields a straight line of slope, $-\log (1+V_w/V_s.K_{ow})$. If the volume of each phase is known, K_{ow} can be calculated from the slope. A straight line is confirmation of a satisfactory experimental technique. Analysis of the water phase is not necessary, neither is absolute concentration measurement in the solvent phase. Only relative concentrations need be measured.

2.4 Estimation Methods

Several solvents may be suitable for a given extraction. Information about the functional groups in both the solute and the solvent and empirical knowledge of extraction systems can help to narrow the possibilities. For example, branched solvents are reported as being more effective than their straight chain counterparts (Munson and King, 1984). Lower molecular weight solvents have been found to be more effective than higher molecular weight solvents with the same general structure (Barbari and King, 1982). Lewis acid-base interactions and hydrogen bonding also affect separations (Joshi, Senetar and King, 1984). However, a large number of solvents may still be

suitable for any given application. Determination of the thermodynamic values of selectivity and capacity for each possible solvent would involve extensive laboratory measurements of equilibrium partitioning and activities. Hence, several attempts have been made to estimate activity coefficients and partition coefficients. These values are also of interest in applications such as distillation and azeotropic and extractive distillation.

Equations to correlate liquid-liquid equilibrium data for multicomponent systems using data aquired from binary systems have been developed (Ashton, McDermott and Brench, 1983). These include the Wilson equation, the NRTL (nonrandom two liquid) equation and the UNIQUAC (Universal quasi-chemical) equation. All three equations correlate existing data well but there remains a need to predict the activities for systems not specifically included in the data base.

Activity coefficient estimation methods such as ASOG (analytical solution of groups) (Pierotti et al., 1959, Wilson and Deal, 1962) and UNIFAC (UNIQUAC functional-group activity coefficient) (Fredenslund et al., 1975) incorporate parameters which depend on the structure of the solvents and solutes. Despite reasonable agreement between estimated and experimental values, the use of the ASOG method is not widespread, hence applications of the method have not been developed. UNIFAC, on the other hand, has been expanded from an initial set of parameters based on vapour-liquid equilibrium (VLE) data to include parameters from liquid-liquid equilibrium (LLE) data as well (Magnussen et al., 1981). The choice of which parameters to use depends on the conditions at which the systems are being considered.

The UNIFAC equations can be used to estimate the activity coefficient at infinite dilution, in a binary system or in a ternary system. Although it is found to be a fairly accurate estimation method for the activity coefficient (Campbell and Luthy, 1985, and Dallos and Ratkovics, 1984), UNIFAC is not a substitute for experimental determination of partition coefficients, hence the properties of the most promising solvents should be confirmed experimentally before designing a specific system.

2.5 Other Selection Criteria

Several other properties can influence solvent selection such as cost, toxicity, availability, flammability, safety, waste disposal considerations, process compatibility (Hampe, 1986) and certain physical and chemical properties which are discussed below.

The boiling point, vapour pressure, enthalpy of vaporization and specific heat capacity of a solvent all affect the solvent recovery process. Less heat is required if the solute is recovered in the overhead so a high boiling solvent is sometimes preferable. However, if the solvent is not thermally stable, it can suffer deterioration after repeated use. The solvent should be chemically inert since any reaction with the solute will hinder solvent recovery. However, some processes operate on the principle of an easily reversible chemical reaction, in which case reactivity is encouraged (Sharma ,1983). Solvents should have minimal impurities since these often build up over time and can reduce the solvent effectiveness. The density difference between the extract and the raffinate, the viscosity and the interfacial tension affect the fluid dynamics in the extraction apparatus. A large density difference is desirable for easy phase separation. Low viscosity and interfacial tension promote better mixing with a lower energy requirement. Low interfacial tension systems have a reduced tendency to coalesce. Therefore, with equal energy input, a system with a lower interfacial tension will have a larger area available for mass transfer than a system with a higher interfacial tension. Excessively low interfacial tensions may cause emulsion formation.

2.6 Liquid Extraction Equipment

Various types of extraction units are described in the literature (Pratt and Hanson, 1983). The choice of a given extractor depends on the application. In this case, a stream of contaminated water containing a range of organic compounds at concentrations which may vary over time must be treated. The extractor must be able to handle low solvent to water flowrates and must be easily cleaned and maintained. The design must permit the easy transportation to, and set up at, a spill site. From the selection process suggested by Pratt and Hanson (1983), a raining bucket contactor, a rotary disk contactor, an agitated mixer settler or a reciprocating plate column appear suitable.

The raining bucket contactor has a horizontal shaft which is rotated within a stationary cylindrical vessel. It has a series of plates upon which are mounted buckets open to the direction of rotation. The two phases flow countercurrently through annular gaps between the rotating plates and the vessel. The buckets pick up one phase and then disperse it through the next phase during a rotation. The design is ideal for systems with low interfacial tension requiring little energy for

dispersion. The contactor can easily handle phase ratios ranging to 1/6 but requires design modifications to accommodate S/W ratios as low as 1/20 (Coleby, 1983). Due to these limitations, the raining bucket contactor is not considered further in this study, it being expected that very low S/W ratios will be desirable.

Rotary disk contactors include the rotating-disk contactor, the asymmetric rotary disk contactor, the Scheibel column, the Khuni extraction column and the Oldshue-Rushton column. Each column has subtle variations but all consist of a series of plates which rotate along a vertical shaft to impart energy to the liquid, thus enhancing mixing and mass transfer. Applications for the rotary disk contactors include processes which require a long residence time or a large number of equilibrium stages, and treatment for non-emulsifiable materials. Backmixing is significant in columns of larger diameter (ie. full scale) and the related loss of efficiency must be taken into account during scale up (Kosters, 1983). This type of column operates with adequate capacities at low S/W ratios and may be suitable for this application provided stable emulsions are not formed.

A mixer settler is a series of compartments through which two phases are mechanically agitated and then allowed to settle. The solvent and water flow countercurrently from each stage. Mixer settlers can handle large flows (up to hundreds of cubic meters per hour) (Godffrey and Slater, 1983) but the number of stages required increases exponentially as the required removal efficiency increases. If the K_{ow} of a solvent is very high (ie. greater than 1000), mixer settlers would be suitable since only one or a few stages would be required for the extraction.

A reciprocating plate column is a countercurrent contactor in which a vertical shaft equipped with a series of plates and baffles oscillates at a selected amplitude and frequency (Karr, 1959). The reciprocating motion of the plates provides energy to the dispersed phase causing it to be broken into fine droplets providing a large interfacial area for mass transfer. In the Karr reciprocating plate extraction column the plates have a large open area (54-65%) and large holes (16 mm) (Lo and Prochazka, 1983, Karr, 1980). This configuration eliminates the need to have plates which fit snuggly into the column since channelling will not be a problem.

The RPC offers several advantages for the spill clean up application, the first being that the column can operate at a large throughput for a given cross sectional area (Lo and Prochazka, 1983). The column is versatile and flexible. It can accomodate solvents which are either more or less dense than water and it can easily be adapted for a feed to the middle of the column for a dual solvent system. Flowrates can fluctuate without greatly affecting removal efficiencies. The plate

suspended solids. The operation of the column is straight-forward and maintenance requirements are low. The column can be constructed from a wide range of materials to suit nearly any application. Finally, the RPC can operate at low solvent to water flow ratios which are desired for solvents with a high capacity (Mackay and Medir, 1977).

Mass transfer within the column can be optimized by adjusting either the throughput to the column or the intensity of agitation or the plate spacing. At higher throughputs, the efficiency of the column decreases (Karr, 1959). Changing either the frequency or the amplitude of reciprocation affects the agitation within the column. An increase in agitation causes a finer dispersion of droplets, hence increasing the area available for mass transfer. The plate spacing should be adjusted to maintain an even dispersion throughout the length of the column. As the solute concentration increases in the column, the interfacial tension of the system decreases, as does the energy required for mixing. Since the reciprocating frequency is constant at all points within the column, the plates are generally placed further apart in the sections of the column in which the solute concentration is high, to reduce the energy imparted to the liquid at that point (Karr, 1959, Lo and Prochazka, 1983). Each of the above parameters is limited by the flooding point in the column. For the purposes of this study flooding is considered to occur when the dispersed phase is visibly entrained in the outlet of the continuous phase. The entrainment can be eliminated by reducing the frequency of agitation or the throughput to the column. The plate material can also affect mass transfer if the dispersed phase coalesces on the plates (Jares and Prochazka, 1987, Shen et al., 1985).

For columns with larger diameters, axial mixing becomes a concern (Karr et al., 1987, Pratt and Baird, 1983) since it reduces the efficiency of the column. To reduce the effects of back mixing, baffles are placed periodically in the plate stacks of larger diameter columns. Karr (1980) recommends that a baffle plate be placed in every sixth position.

In view of its simplicity, flexibility and good performance it is believed that the RPC is the most suitable for a mobile unit as considered in this study. Accordingly, the experimental program and design treat this type of contactor.

2.7 Scale-up of the Reciprocating Plate Column

In order to design a full scale RPC, pilot scale tests should be conducted to determine optimum throughput, agitation frequency and amplitude and plate spacing. Measurements are made to determine the HETS (height equivalent to a theoretical stage) at various throughputs. For small diameter columns the minimum HETS will occur at a frequency which is reduced by 5-10% from the frequency at which flooding occurs (Lo and Prochazka, 1983). In general, HETS will increase as the throughput is increased.

A value for the HETS can be calculated from the height of the column, Z, and the number of theoretical stages for the column, N (Robbins, 1984):

$$HETS = Z/N \qquad [2\text{-}9]$$

The number of theoretical stages can be determined graphically from a McCabe-Thiele diagram (Figure 2.2). The equilibrium line is given by:

$$Y = K_{yx}.X \qquad [2\text{-}10]$$

where,

Y is the mass ratio of the solute in the solvent (g solute/g solvent), and

X is the mass ratio of the solute in the water (g solute/g water).

K_{yx} is equal to K_{ow} multiplied by the ratio of the densities of the two phases, (ρ_w/ρ_s).

The slope of the operating line is the ratio of the water feed flow, W, to the solvent flow, S, both in mass/time units.

For a system with a straight equilibrium line with a zero intercept and a straight operating line, the number of theoretical stages for a countercurrent contactor can be calculated by the Kremser equation:

for $e \neq 1.0$

$$N = \ln[(X_f - Y_s/K_{yx})/(X_r - Y_s/K_{yx}).(1-1/e)+1/e]/\ln e \qquad [2\text{-}11]$$

for $e = 1.0$

$$N = [(X_f - Y_s/K_{yx})/(X_r - Y_s/K_{yx})]-1 \qquad [2\text{-}12]$$

where,

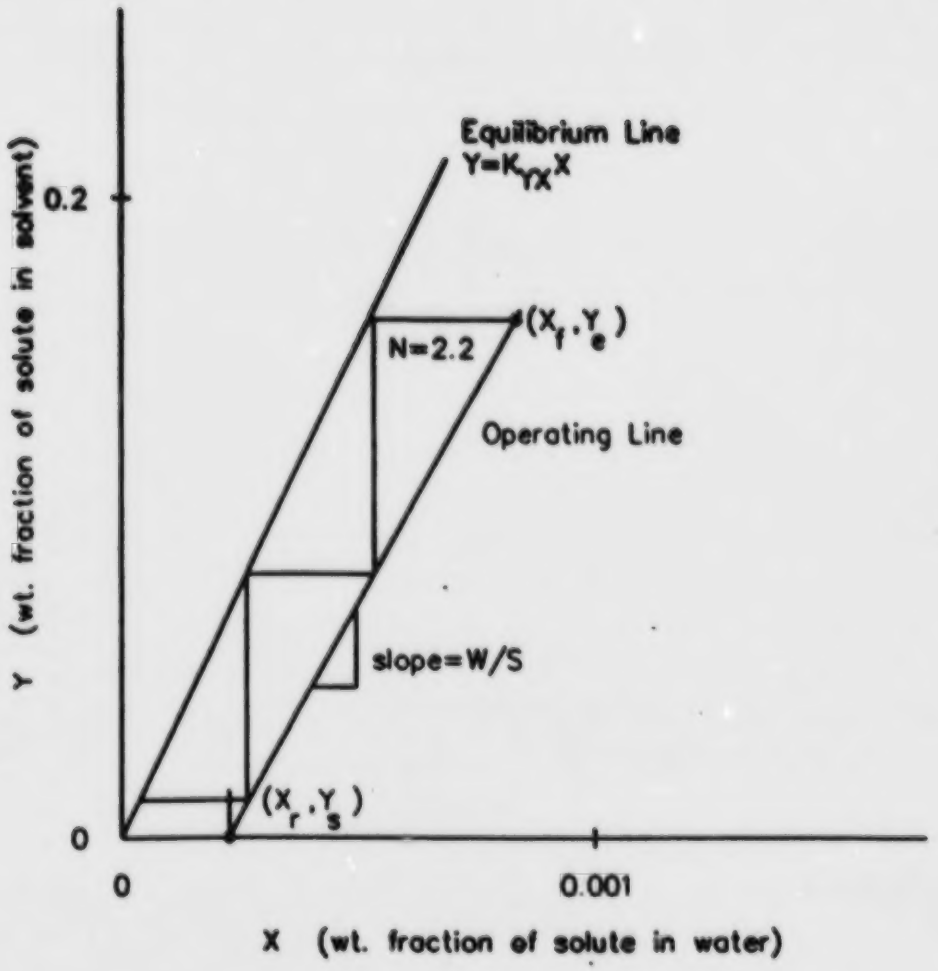


Figure 2.2 Typical McCabe-Thiele Diagram for a Continuous Countercurrent Liquid Extraction Column with Water Feed

e is the extraction factor and is equal to the slope of the equilibrium line, divided by the slope of the operating line, that is,

$$e = K_{yx}.S/W \qquad [2\text{-}13]$$

The subscripts f, s and r refer to the water feed, solvent feed and raffinate streams, respectively. Alternatively, graphical stepping construction (i.e. as in Figure 2.2) is possible.

For scale up from pilot scale tests, the total throughput per unit area, the plate spacing and amplitude are maintained (Karr et al., 1987). The HETS for the full scale system will increase according to:

$$(HETS)_2/(HETS)_1 = (d_2/d_1)^n \qquad [2\text{-}14]$$

where

(d_2/d_1) is the ratio of the diameter of the full scale unit to the diameter of the pilot scale unit, and

n has been found to be 0.38 for difficult extractions and decreases for easier extractions.

The frequency, f of agitation will decrease according to:

$$f_2/f_1 = (d_2/d_1)^{-0.34} \qquad [2\text{-}15]$$

The scale up equations assume plug flow, neglecting axial mixing. Although this is not accurate it is believed to be sufficient for the design of a system intended to be used on a variety of different feeds using different solvents. Models which take axial mixing into account are more complex and are not judged to be necessary for this application.

2.8 Solvent Recovery

For LE systems to be economical, the solute must be recovered from the solvent (Robbins, 1980, Mackay and Medir, 1977). The process used depends on the properties of the compounds involved and can include a second extraction process, distillation or steam stripping. For steam stripping, (which is considered in detail in this study) the solute should have a lower boiling point than the solvent since energy requirements are lower if the solute is recovered in the overhead. The output of a steam stripper is a condensate stream containing water and solute and a second stream of clean solvent. The condensate may require further treatment since it will contain a high

concentration of the solute. Therefore the recovery process will only be justified if the volume of condensate produced is considerably less than the original volume of water treated.

The volume of steam required for the removal of a given solute can be estimated from a mass balance on the steam stripper (Figure 2.3). The process is a semi-batch operation in which the solvent is contained in a heated vessel through which steam flows. The steam rises to the top of the unit and passes through a condenser to a collection vessel. The mass balance for solute i, yields:

$$V_s \, dC_{is}/dt = -F_v C_{iv} \qquad [2\text{-}16]$$

where,

V_s is the volume of solvent to be stripped (m^3),

C_i is the concentration of the solute (g/m^3),

t is time (h),

F_v is the flowrate of the steam vapour (m^3/h), and

s and v indicate the solvent and steam vapour phases.

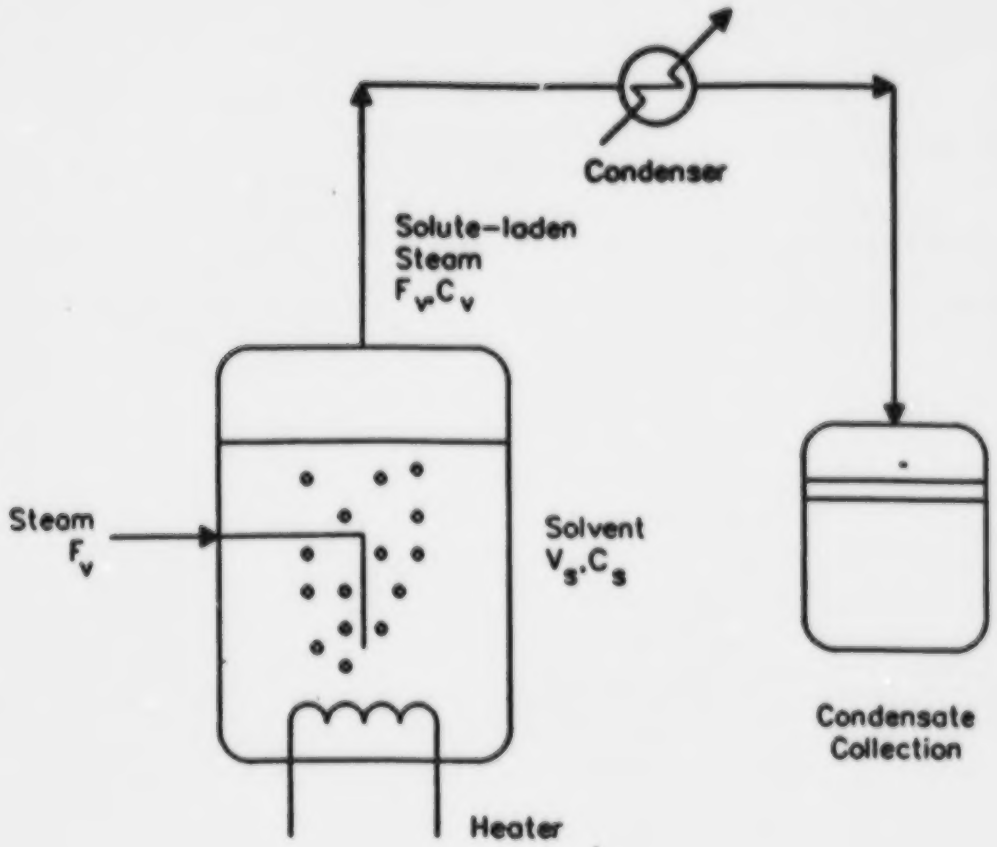


Figure 2.3 Schematic of Steam Stripping Apparatus

To solve the differential equation, C_w is related to C_v. At equilibrium, the fugacities of the two phases are equal, and

$$x_i \gamma_i P_i^s = P_w \qquad [2\text{-}17]$$

where,

x_i is the mole fraction of the solute in the solvent,

γ_i is the activity coefficient of the solute in the solvent,

P_i^s is the vapour pressure of the solute (Pa) and

P_w is the partial pressure of the solute in the vapour phase (Pa).

By expressing the mole fraction in terms of concentration units and by assuming that the vapour acts as an ideal gas, [2-17] becomes:

$$C_w MW_s \gamma_i P_i^s / 1000 \rho_s = C_v R T \qquad [2\text{-}18]$$

where,

MW_s is the molecular weight of the solvent (g/mol),

ρ_s is the density of the solvent (kg/m^3),

R is the Universal Gas Constant (8.314 Pa·m^3/mol·K) and

T is the absolute temperature in the stripping apparatus (K).

Therefore,

$$C_v = K_w C_w \qquad [2\text{-}19]$$

where, K_w is the vapour/solvent partition coefficient given by

$$K_w = MW_s \gamma_i P_i^s / (1000 \rho_s R T) \qquad [2\text{-}20]$$

then equation [2-16] becomes,

$$V_s dC_w/dt = -F_v K_w C_w \qquad [2\text{-}21]$$

with the solution for a solvent of initial concentration C_w°,

$$\ln(C_w/C_w^\circ) = -F_v K_w t / V_s \qquad [2\text{-}22]$$

For a desired reduction in the concentration of the solute in the solvent, the volume of steam required in a given time can be estimated. For example, for 99% removal of solute the right hand

side of [2-22] must equal 4.6, thus the total volume of steam (F,t) must be $4.6/K_w$ times the volume of solvent treated. Clearly, K_w should be as large as possible, implying that the solute should have a large vapour pressure. A volatile solvent with a vapour pressure of 30000 Pa at the stripping temperature would have a K_w of approximately 0.01, thus 460 volumes of steam would be required.

2.9 Other Processes

The literature also contains discussions of several processes related to solvent extraction which may or may not be effective for organic compounds in water. For example, in supercritical fluid extraction (Hoyer, 1985, Brogle, 1982 and Ehntholt, Eppig and Thrun, 1987) the solvent (usually CO_2) is kept at a high pressure so that extraction occurs in the supercritical region. Although the use of non-toxic CO_2 as a solvent is attractive for environmental purposes, the method is only effective for sparingly soluble, volatile organics. A membrane process using solvent extraction principles has also been suggested (Prasad and Sirkar, 1987). Another alternative is the use of a predispersed solvent to extract solutes from water (Sebba, 1985).

2.10 Summary

In summary, the feasibility of LE for the removal of organic compounds from water has been reviewed and is best assessed by laboratory scale and pilot scale experiments. The equilibrium partition coefficients, K_w, can be measured by one of two techniques, both of which are investigated. The first involves the analytical determination of the solute concentration in both the water and solvent phases, to calculate the ratio of the two concentrations. The second method consists of sequentially extracting a small volume of solvent which contains solute with a large volume of water. The K_w can be estimated from the decrease in solute concentration in the solvent at each extraction stage.

A pilot scale reciprocating plate extraction column is operated under varying conditions to assess LE on a larger scale. Steam stripping is investigated as a method for solvent recovery. Data from the pilot scale is used for a preliminary design of a full scale mobile unit.

3. Experimental Methods

3.1 Partition Coefficient Measurements

Choice of Solvents and Solutes

The choice of solvents for the experimental determination of partition coefficients was guided by a need to cover a range of chemical structures and properties (Table 3.1). Dichloromethane is frequently used as a solvent for analytical extractions. It is a small molar volume compound and not subject to steric hindrances. However, it does have a high solubility in water which may reduce its suitability. Ethylbenzene is representative of aromatic compounds. N-octane represents straight chain hydrocarbons, and should indicate the effectiveness of petroleum derivatives as solvents. N-octanol is chosen for comparison with the extensive literature values for partition coefficients between octanol and water as well as a representative of the hydroxyl functional group. For analytical reasons it was decided to use pure solvents.

In choosing the solutes, it was desirable to include a cross-section of functional groups and chemical properties which are commonly encountered in spill situations (Table 3.1). Acetone represents ketones; toluene, ethylbenzene and 1,2-dichlorobenzene are substituted aromatics; and chlorinated aliphatics are represented by 1,2-dichloroethane and 1,1,2,2-tetrachloroethane.

Sample Preparation

Measured volumes of the solvent and water were added to erlenmeyer flasks with teflon coated septums and screw caps. All laboratory samples were prepared using distilled-deionized water. The solute was added either by pipette or by gas-tight syringe to the bottom layer in the flask to minimize solute losses by volatilization. Three concentrations of solute were considered for each system. The amount of solute added was kept as low as possible while maintaining a concentration in the water phase which could be quantitatively determined.

Table 3.1 Chemical and Physical Properties of the Solutes and Solvents[a]

Compound	Formula Weight (g/mol)	Boiling Point (°C)	Vapour Pressure (kPa)[b]	Density (g/cm^3)[c]	Solubility (g/m^3) (at °C)	Water Uptake (mass %)
acetone	58.08	56.2	36	0.791	miscible	
1,2-dichloro-benzene	147.01	179	0.25	1.305	100 (20) 145 (25)	
1,2-dichloro-ethane	99	83.5	14	1.25	8690 (20) 9200 (0)	
dichloro-methane	84.93	40-42	66.7	1.336[d]	20000(20) 16700(25)	0.198[e]
ethylbenzene	106.17	136.2	1.6	0.867	140 (15) 152 (20)	0.043[e]
n-octane	114.23	125.7	2.4	0.7	0.66(20)[e]	0.0095[e]
1-octanol	130.23	195	0.13[f]	0.824	300 (20)	5.9[g]
toluene	92.1	110.8	5.3	0.867	470 (16) 515 (20)	
1,1,2,2-TeCE	167.86	146.4	1.1	1.60	2900 (20)	

a. K. Verschueren, 1977, except where noted.
b. at 30°C, except where noted.
c. at 20°C.
d. P.E. Liley, et al., 1984.
e. Hampe, 1986.
f. at 54°C.
g. Leo, Hansch and Elkins, 1971.

The flasks were stirred to equilibrium by a magnetic stirrer for a minimum of 1-2 hours. The stirring speed was low enough that the interface between the two phases was not disturbed. This reduced the possibility of emulsion formation. The flasks were maintained in a temperature controlled water bath for a minimum of 8 hours before sampling. The partition coefficients were measured at three temperatures, namely, 5°C, 15°C and 25°C.

Analysis

Sample analysis was performed on two Hewlett Packard gas chromatographs (GC). The solvent phase analysis was done on an HP 5750 GC equipped with a 3 m long, 3.2 mm O.D. packed column (10% SE-30 U.P. silicone packing) and a flame ionization detector (FID). Helium was used as a carrier gas and the FID flame was fueled by a hydrogen and air mixture. The volatile organics in the water phase were analysed by an HP 5840A GC with an HP 7675A Purge and Trap Sampler equipped with a 30 m DB-1 column and an FID detector. The carrier gas was nitrogen and the flame was fueled by a hydrogen and air mixture.

Non-volatile compounds could not be analysed by the purge and trap method, instead, they were analysed by direct injection on the packed column GC. Since the concentration in the water phase was too low to detect on the FID, the samples were concentrated by extraction with hexane. Twenty-five mL of water was removed by pipette and was extracted with 0.5 mL of hexane. The water was decanted and the hexane phase analysed in the same manner as the other solvent phases. Periodically, a second extraction was performed to determine the extraction efficiency of the hexane. If the extraction was not complete, the average efficiency was taken when calculating the concentration of the solute.

The solute concentration was quantified by calibrating the GC with external standards. For the packed column GC, standards were prepared in the solvent at different dilutions. Several injections were made at different volumes to cover the range of expected areas. A calibration line using at least five points related the area detected to the amount of solute present in the injected sample. Since the area of solute was independent of the solvent used, some standards are prepared in hexane only, while others were prepared in the individual solvents. For the purge and trap GC, standards were made by successive dilutions of a saturated water solution until concentrations representative of those in the water phase of the samples were obtained. Again a calibration line with at least five points was determined. For both GCs, daily calibration checks were made to ensure that the detection sensitivity did not drift.

3.2 K_{ow} Measurement by Sequential Extractions

Although this method was devised so that the water phase did not have to be analysed, the analysis was done in order to compare the values of K_{ow} determined by each technique. A 20 mL sample of Isopar M was "spiked" with both toluene and 1,1,2,2-TeCE. Ten milliliters were mixed with 1L of distilled-deionized water in a separatory funnel. The two phases were allowed to separate. A weighed sample of water was extracted with hexane and the hexane phase was analysed. The remaining water was decanted and the solvent phase was anaylsed. Fresh water was added to the separatory funnel and the process was repeated until at least five extractions were completed. Analysis of all samples was done on the packed column GC.

3.3 Pilot Scale Experiments

Choice of Solvent and Solutes

The solvent requirements for the operation of a full scale unit are different from those of the partitioning study. The solvent must have a low toxicity so that a larger pollution problem is not created during cleanup of a spill. It should provide adequate extraction for a wide range of organic compounds and should have a low flammability so that it can easily be handled safely at a spill location. Based on these criteria and the suggestion of Professor M. H. I. Baird, of McMaster University in Hamilton, Ontario, Isopar M was chosen as the solvent for the pilot scale experiments. It is a petroleum distillate fraction in the range of C_{11}-C_{13} manufactured by Esso Chemical Canada. The relevant chemical properties are given in Table 3.2. Figure 3.1 shows a GC trace of Isopar M on a capillary column. The peaks are marked with the appropriate carbon numbers.

Table 3.2 Properties of Isopar M[a]

Boiling point range:	Initial boiling point	206°C
	Final boiling point	256°C
Density at 15°C	0.792 g/cm^3	
Vapour Pressure at 38°C	0.2 kPa	
Viscosity at 25°C	2.42 cP	
Flash Point (closed cup)	79°C	

a. Source is product data sheet provided by Esso Chemical Canada.

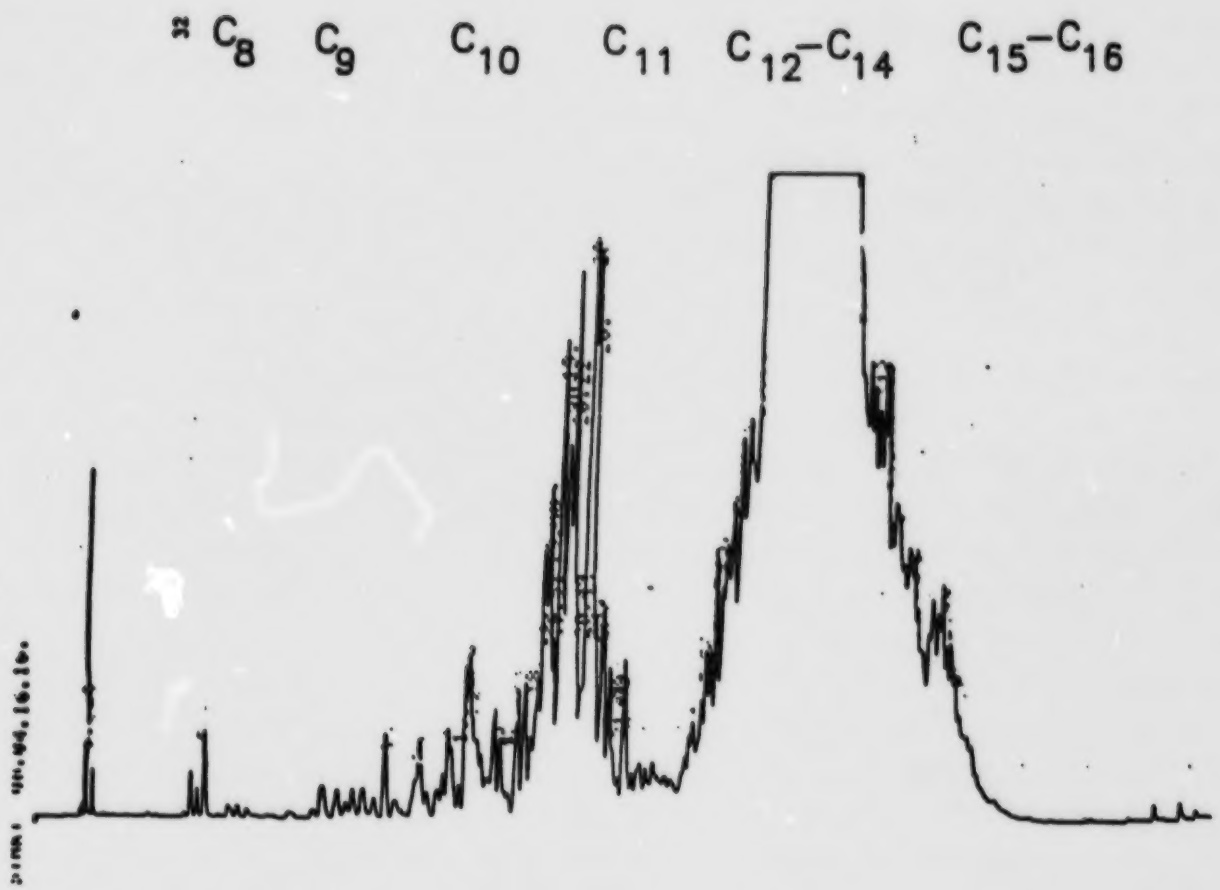


Figure 3.1 Chromatogram of Isopar M on a Capillary Column GC

It was not feasible to test all six solutes in the pilot scale tests. Two test chemicals were selected to reflect a range of the chemical properties listed in Table 3.1. The choice was aided by the obvious disqualification of several solutes. Due to the extremely low K_{ow} value, acetone was considered to be unsuitable for extraction from the water phase by the solvents considered. The retention time of 1,2-dichlorobenzene coincided with the retention time of some Isopar M peaks. Although this would not affect the extraction process, it does prevent the quantitative analysis of the solute in Isopar M. From the remaining solutes, toluene and 1,1,2,2-tetrachloroethane were chosen. The equilibrium partition coefficients for the two test chemicals in Isopar M were determined by consecutive extractions of spiked Isopar M solutions with pure water, as described in section 3.2.

Reciprocating Plate Column Apparatus

The experiments were performed on a 2.5 m high, 5.0 cm inner diameter RPC shown schematically in Figure 3.2. The column is manufactured of borosilicate glass with neoprene gaskets and PTFE feed rings and terminal plates. The reciprocating plates and shaft are of stainless steel. Twenty-five plates were used with spacing ranging from 2.5 to 7.5 cm for a total plate height of 125 cm (Figure 3.3). The solvent was fed to the base of the column from a constant gravity overhead tank. The contaminated feed was fed directly, by centrifugal pump, to the top of the column. Samples of the water inlet and outlet and solvent outlet were taken at timed intervals throughout each run.

The feed was prepared by adding an appropriate volume of the two solutes to the feed tank and mixing the solution with a submersible pump for several hours. A teflon sheet was placed over the water to reduce volatilization of the solutes and hence maintain a constant feed concentration.

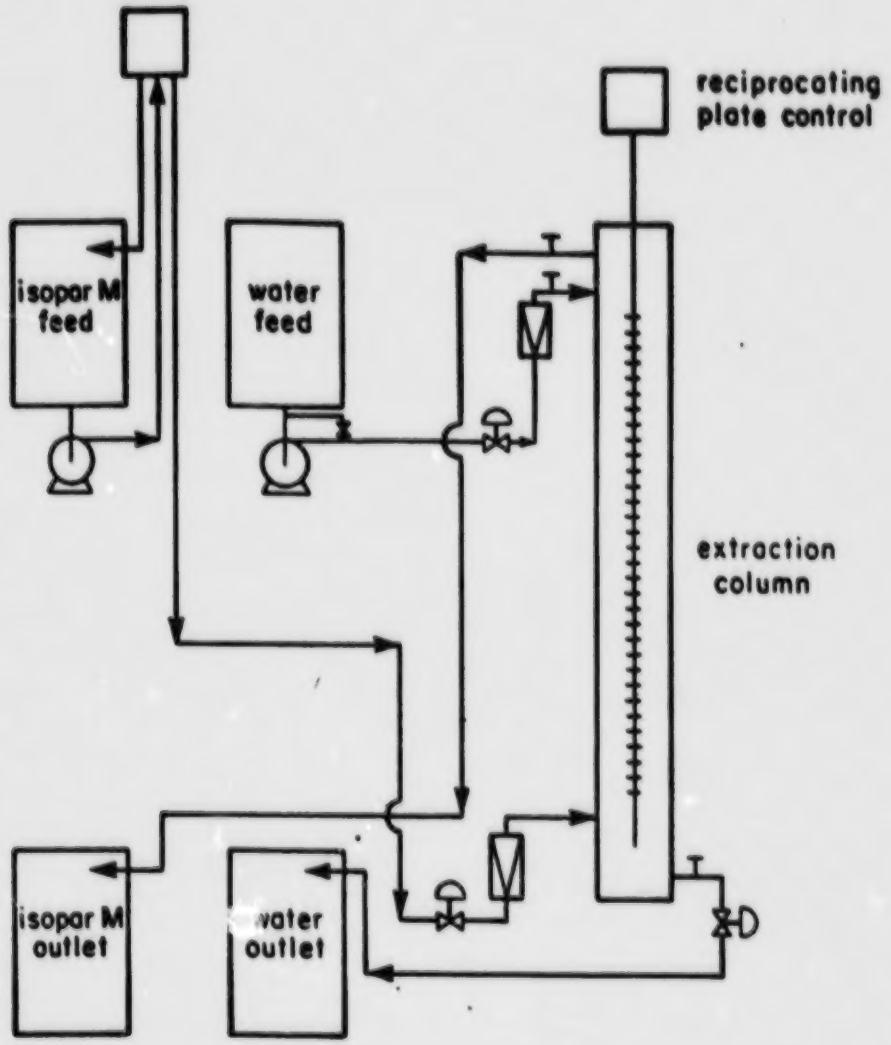


Figure 3.2 Schematic of the Pilot Scale Reciprocating Plate Column

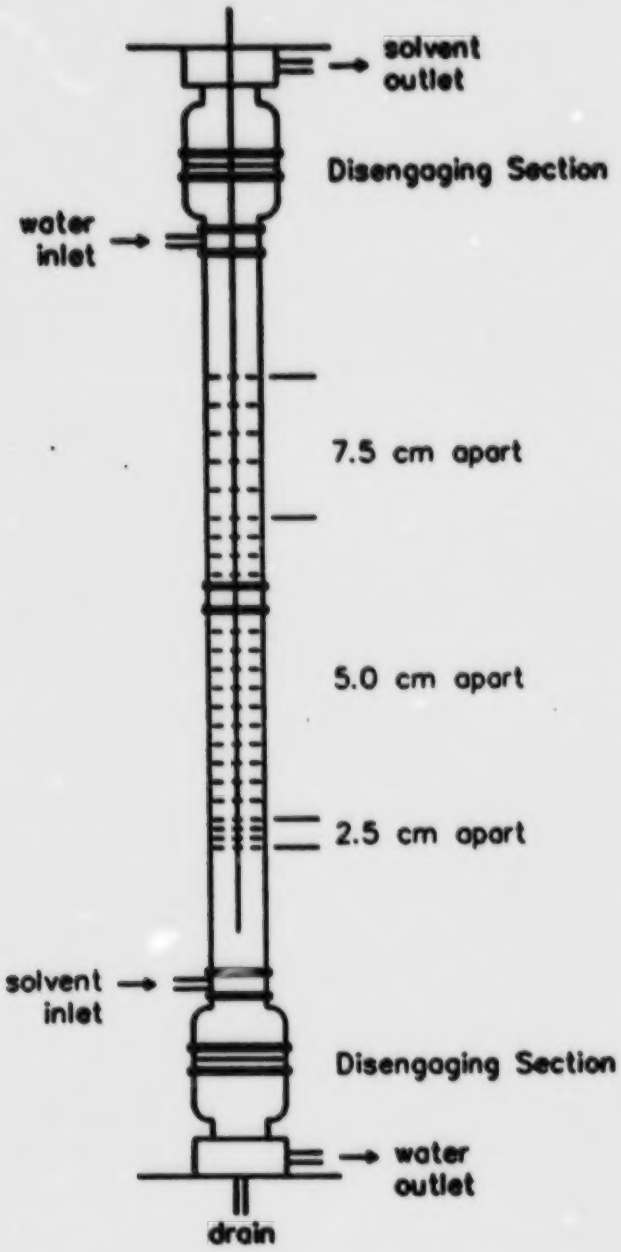


Figure 3.3 Diagram of Extraction Column Showing Plate Spacing

Analysis

The water samples were collected in weighed vials containing 2.0 mL of hexane. The vials were reweighed to determine the volume of water in each sample (approximately 50 mL). The hexane phase was analysed directly from the bottles. Second extractions were performed by removing 25 mL of the water phase for extraction with 0.5 mL of hexane. The average extration efficiency for each solute was considered when calculating the water concentration. The solvent samples were taken in vials sealed with a teflon coated cap. All samples were analysed by direct injection to a packed column GC. Duplicate samples were taken, but only one was analysed unless a questionable value was obtained.

The accuracy and precision of the water sampling technique was estimated by the following procedure which attempted to mimic the actual sampling technique. Four water standards were prepared from saturated water solutions to contain 5 g/m^3 and 50 g/m^3 toluene and 300 g/m^3 and 900 g/m^3 TeCE. Approximately 50 mL of each standard was transfered by pipette to six weighed vials containing 2.0 mL hexane. The 48 vials were reweighed and each hexane phase was analysed. Second extractions were performed as previously mentioned. Accuracy is defined as the percent difference between the expected concentration and the measured concentration. Precision is indicated by the standard deviation of the average concentration of all injections for the six samples.

3.3 Steam Stripping

Although both distillation and steam stripping are suitable processes for solvent recovery, steam stripping is perceived as the safer alternative and is examined in this study.

Steam Stripping Apparatus

Steam stripping of the solvent was carried out in a semi-batch operation (Figure 2.3). The solvent was contained in a heated 60 L glass vessel through which steam flowed. The steam was condensed in an overhead condenser and the condensate was cooled further in an ice-jacketed vessel. The steam flow rate was calculated by collecting timed volumes of condensate. Samples of the solvent were taken from the vessel at 30 minute intervals.

Analysis

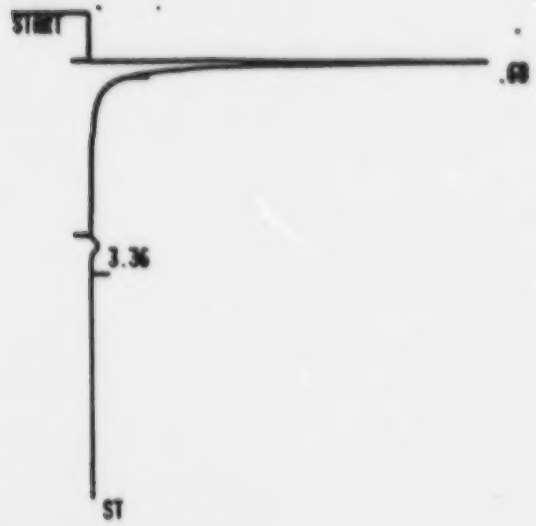
The solvent samples were analysed by direct injection to the packed column GC. The aqueous phase of the final condensate sample was analysed by hexane extraction. The organic layer floating on the aqueous condensate was analysed directly.

4. Results

4.1 Partition Coefficient Measurements

The concentration of the solute in both phases was quantified from peak areas on GC chromatograms. The calibration lines for each solute are given in detail elsewhere (Adams, 1989). Each calibration line was linear with a correlation coefficient (r^2) greater than 0.9. Some solutes were calibrated using two or more solvents depending on when the systems were analysed. For example, toluene and 1,2-DCE were calibrated at different times in octane, ethylbenzene and DCM, while 1,2-DCB was calibrated only in hexane. When the two calibrations were made within a few months of each other, reproducibility was within 16% for DCE and within 5% for toluene. However, calibrations made more than a year apart show a decrease in sensitivity by 70%, indicating that the response of the FID was changing and cleaning was required. Selected, typical GC traces are shown in the following six figures.

Figure 4.1 illustrates the acetone peak from a water sample run on the packed column GC. The tailing of the peak is the result of analysing a polar compound on a column designed for non-polar compounds, however, this does not prevent accurate quantification of the solute concentration. The concentration of the acetone in the water was sufficient that the sample could be injected directly to the GC, however, for other solutes, such as 1,2-DCB, the water phase had to be concentrated by extraction with hexane before the solute concentration could be quantitatively determined. The hexane removed 95.4% of the DCB in the first extraction (Figure 4.2) leaving only a small peak in the second extraction (Figure 4.3). The peak at 3.67 minutes in Figure 4.2 indicates the amount of ethylbenzene which had dissolved in the water phase. The concentration of ethylbenzene is approximately 60 g/m^3, well below the solubility of ethylbenzene in water.



RUN # 1267 APR/29/88 15:07:36

AREA%

RT	AREA	TYPE	AR/MT	AREA%
0.68	401170	PB	0.867	95.569
3.36	18600	BB	0.162	4.431

Figure 4.1 Chromatogram of Acetone (RT: 0.68 min.) in Octane (RT: 3.36 min.) and Water, Water Phase

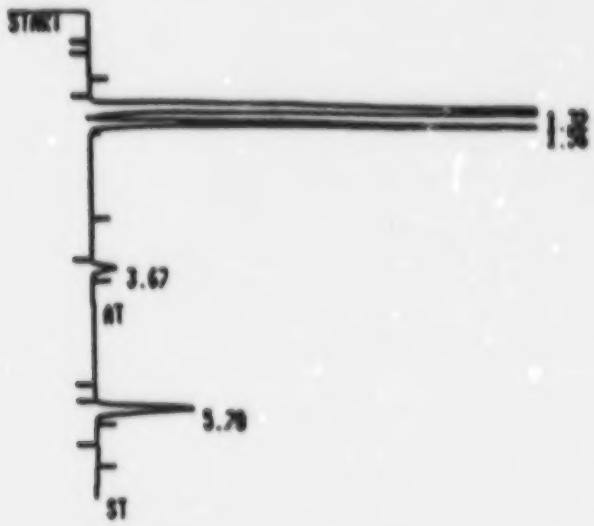


Figure 4.2 Chromatogram of 1,2-DCB (RT: 5.7 min.) in Ethylbenzene (RT: 3.67 min.) and Water, 1st Hexane (RT: 1.32 min.) Extraction of the Water Phase

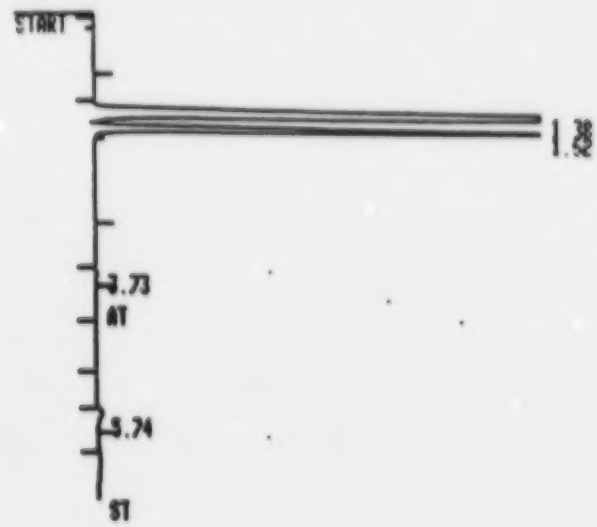


Figure 4.3 Chromatogram of 1,2-DCB (RT: 5.74 min.) in Ethylbenzene (RT: 3.73 min.) and Water, 2nd Hexane (RT: 1.38 min.) Extraction of the Water Phase

Analysis of toluene in octane is shown in Figure 4.4. The water phase for toluene was analysed by purge and trap GC with the resulting chromatogram shown in Figure 4.5. The different retention times for toluene are a result of different carrier gas flow rates, different columns and different temperatures for the two columns. The octane peak in Figure 4.5 (Retention Time: 20.49 minutes) is comparable to the peak for a solution of water saturated with octane (RT: 21.66 min.) (Figure 4.6), indicating that the water sample did not contain excess solvent.

Once the concentration in each phase was known, the K_{ow} and the mass balance were calculated. All data were entered and stored on Lotus 1-2-3 worksheets. Typical results are illustrated in Table 4.1 for the 1,2-DCE-ethylbenzene-water system. The number of significant figures cannot be readily controlled with Lotus so no importance should be placed on the significant figures shown in Table 4.1 or subsequent tables produced on Lotus. The tabulated results for the remaining systems have been presented elsewhere (Adams, 1989). The average K_{ow} for each system at the three temperatures and the overall average K_{ow} for all temperatures are given in Table 4.2.

Figures 4.7 and 4.8 are examples of the temperature dependence of the K_{ow}. The 1,2-DCE-ethylbenzene-water system (Figure 4.7) showed no detectable effects, while the 1,1,2,2-TeCE-octane-water system showed slight variability (Figure 4.8) but no significant differences. Other systems behaved similarly.

The values of K_{ow} were generally constant for the concentration ranges investigated (ie. the plots of concentration in the water versus concentration in the solvent were linear). Even the dichlorobenzene systems for which the highest solute concentration was 25% by volume of the solvent remained linear. This is illustrated in Figure 4.9 for the 1,2-DCB-ethylbenzene-water system. The outlying point is attributed to a high water concentration for the medium concentration sample at 25°C.

Two of the systems involving DCM as a solvent showed non-linearity in the water concentrations. This is illustrated by comparing Figure 4.10 for the toluene-octane-water system with Figure 4.11 for the toluene-DCM-water system at 25°C. Figure 4.12 illustrates the considerable scatter of the data for the ethylbenzene-DCM-water system.

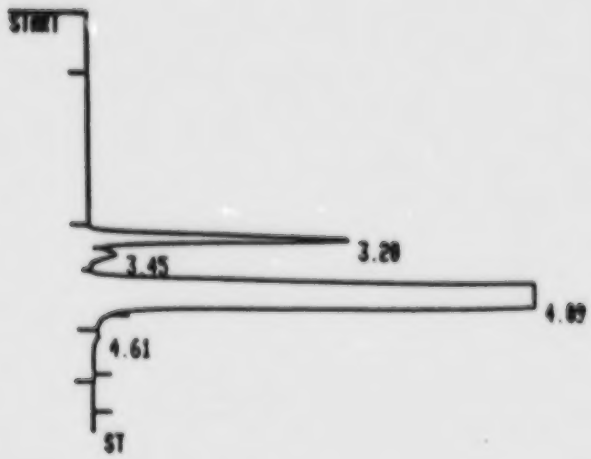


Figure 4.4 Chromatogram of Toluene (RT: 3.2 min.) in Octane (RT: 4.09 min.) and Water, Octane Phase

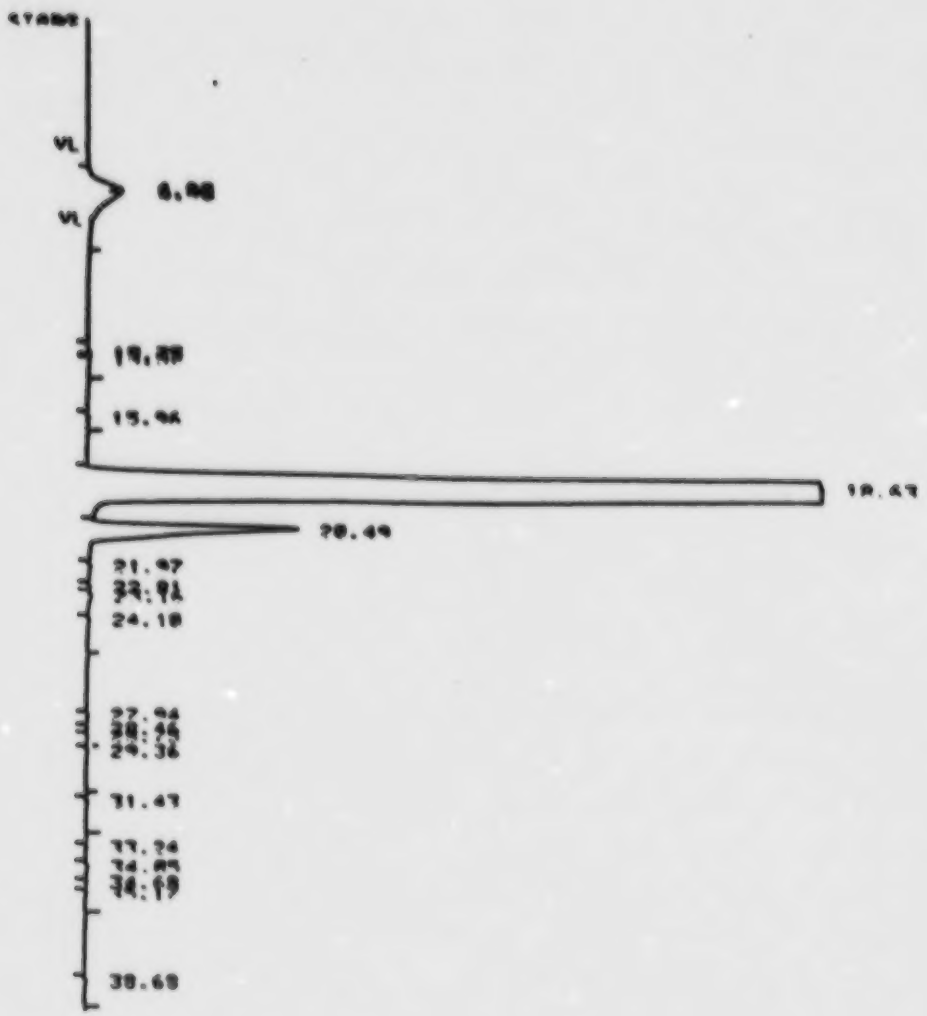


Figure 4.5 Chromatogram of Toluene (RT: 18.63 min.) in Octane (RT: 20.49 min.) and Water, Water Phase

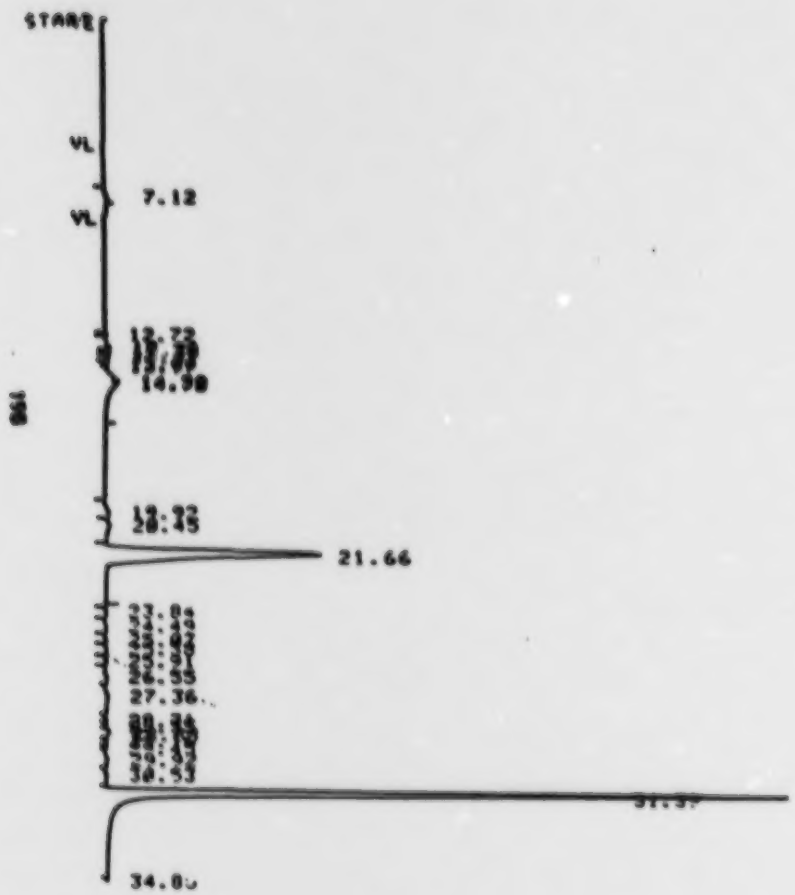


Figure 4.6 Chromatogram of Water Saturated with Octane (RT: 21.66 min.)

Table 4.1 Illustrative Results for the 1,2-DCE-Ethylbenzene-Water System.

volume of water:	50 mL			volume of ethbenz:	50 mL			
		ETHBENZ	WATER		TOTAL	MASS IN	MASS IN	
	SAMPLE	CONC DCE	CONC DCE		MASS	ETHBENZ	WATER	
TEMP (C)	mL	(mg/L)	(mg/L)	Kaw	log Kaw	(g)	(g)	(g)	% DIFF
5	0.75	19116.87	248.53	76.92	1.89	0.94	0.96	0.01	-3.28
	1	27183.82	326.17	83.34	1.92	1.25	1.36	0.02	-10.94
	2	47589.68	654.65	72.69	1.86	2.56	2.38	0.03	3.51
			AVERAGE	77.65					
			SD	4.36					
15	0.75	18345.51	223.66	81.94	1.91	0.94	0.92	0.01	0.96
	1	25479.69	337.91	75.40	1.88	1.25	1.27	0.02	-3.27
	2	45445.42	619.63	70.11	1.85	2.56	2.17	0.03	11.87
			AVERAGE	75.69					
			SD	4.83					
25	0.75	17525.09	229.10	76.50	1.88	0.94	0.88	0.01	5.31
	1	24840.42	321.57	77.25	1.89	1.25	1.24	0.02	-6.65
	2	41693.76	621.29	67.11	1.83	2.56	2.08	0.03	15.37
			AVERAGE	73.62					
			SD	4.61					
		OVERALL AVERAGE		75.74					
			SD	4.80					

Table 4.2 Averages of measured partition coefficients at indicated temperatures, standard deviations in parentheses.

a. AVERAGES AT 5°C
SOLVENTS

SOLUTE	OCTANE	DCM	ETHBENZ	OCTANOL
Acetone	0.07 (0.01)	--	--	--
1,2-DCB	3300 (350)	9040 (1330)	9050 (950)	--
1,2-DCE	15 (1)	130 (4)	78 (4)	23 (2)
Ethylbenzene	--	2600 (660)	--	--
1,1,2,2-TeCE	100 (9)	970 (120)	760 (70)	270 (34)
Toluene	640 (60)	2400 (410)	1100 (55)	595

b. AVERAGES AT 15°C
SOLVENTS

SOLUTE	OCTANE	DCM	ETHBENZ	OCTANOL
Acetone	--	--	--	--
1,2-DCB	3890 (640)	10700(3100)	8740 (610)	--
1,2-DCE	--	170 (8)	75 (5)	--
Ethylbenzene	--	2900 (1080)	--	--
1,1,2,2-TeCE	105 (10)	1360 (130)	780 (87)	230 (15)
Toluene	700 (50)	2420 (75)	1040 (90)	--

c. AVERAGES AT 25°C
SOLVENTS

SOLUTE	OCTANE	DCM	ETHBENZ	OCTANOL
Acetone	--	--	--	--
1,2-DCB	3490 (840)	11700(2400)	7310 (2700)	--
1,2-DCE	--	160 (30)	74 (5)	--
Ethylbenzene	--	5600 (1400)	--	--
1,1,2,2-TeCE	130 (7)	1030 (270)	690 (26)	270 (20)
Toluene	520 (30)	1170 (410)	950 (79)	--

d. OVERALL AVERAGES
SOLVENTS

SOLUTE	OCTANE	DCM	ETHBENZ	OCTANOL
Acetone	0.07 (0.01)	--	--	--
1,2-DCB	3500 (690)	10500(2600)	8400 (1800)	--
1,2-DCE	15 (1)	150 (25)	75 (5)	23 (2)
Ethylbenzene	--	3700 (1700)	--	--
1,1,2,2-TeCE	110 (15)	1120 (250)	740 (77)	260 (30)
Toluene	620 (90)	1990 (670)	1030 (100)	595

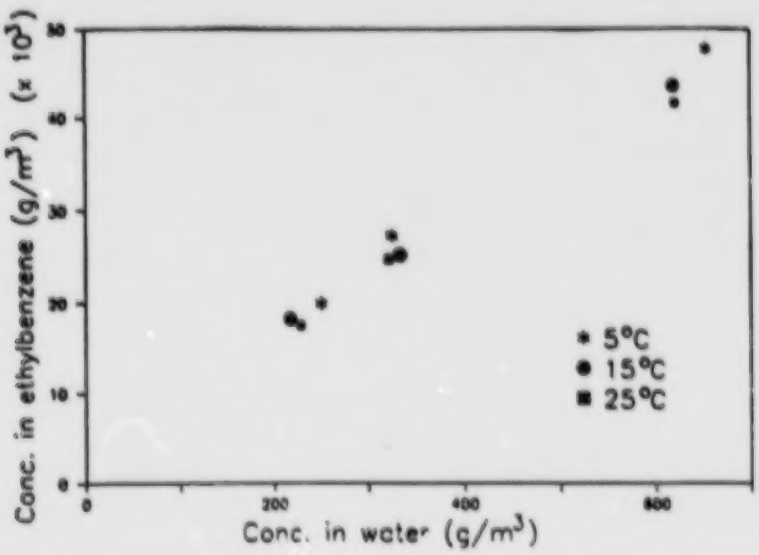


Figure 4.7 Temperature Dependence of K_{ow} as Illustrated by the 1,2-DCE-Ethylbenzene-Water System

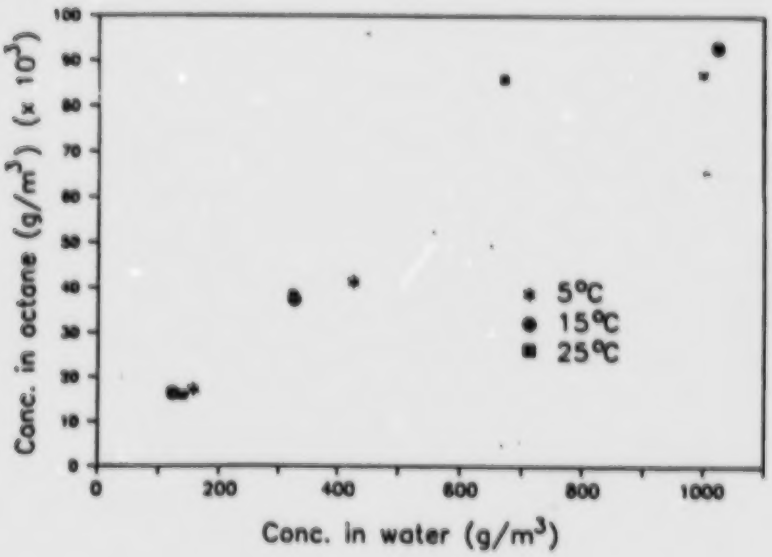


Figure 4.8 Temperature Dependence of K_{ow} as Illustrated by the 1,1,2,2-TeCE-Octane-Water System

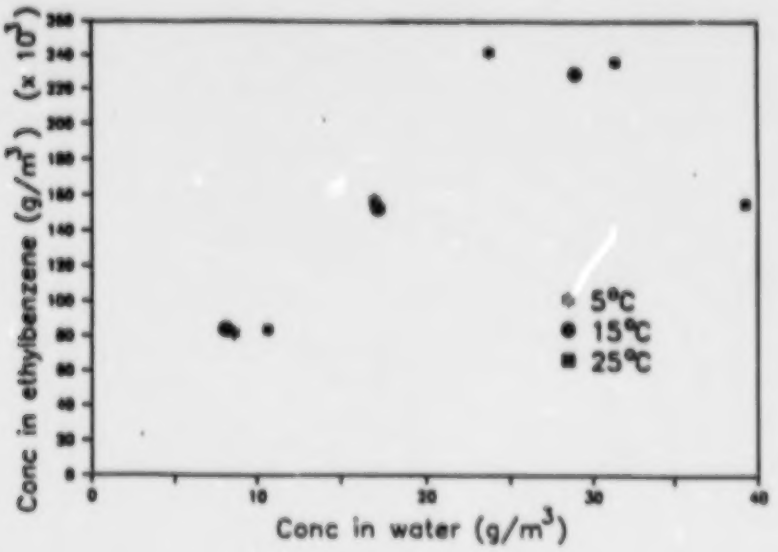


Figure 4.9 Linearity of K_{ow} as Illustrated by the 1,2-DCB-Ethylbenzene-Water System

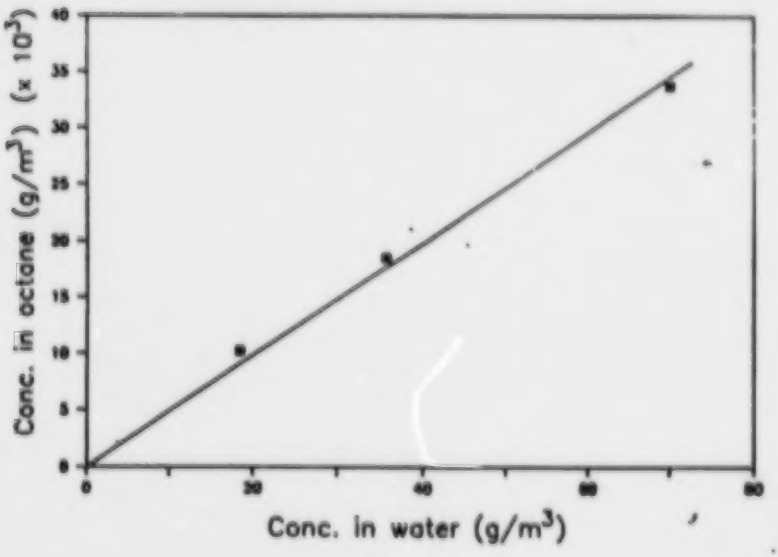


Figure 4.10 Linearity of K_{ow} as Illustrated by the Toluene-Octane-Water System

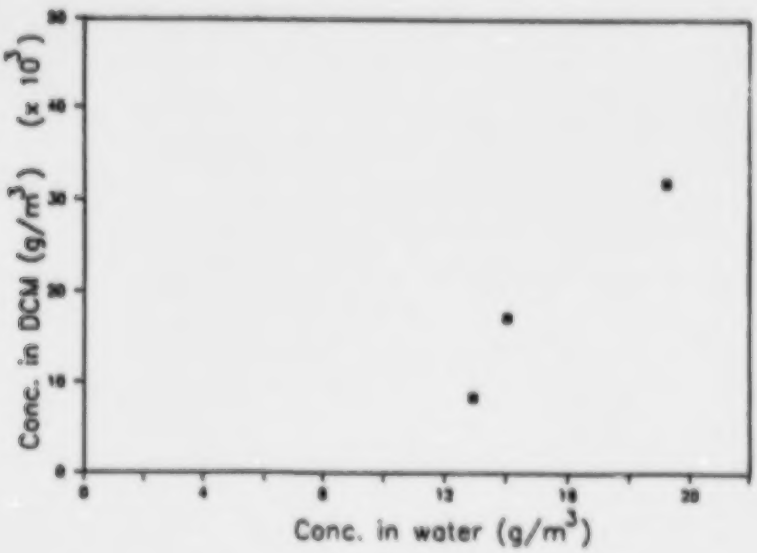


Figure 4.11 Irregularities in the Values of K_{ow} as Illustrated by the Toluene-DCM-Water System

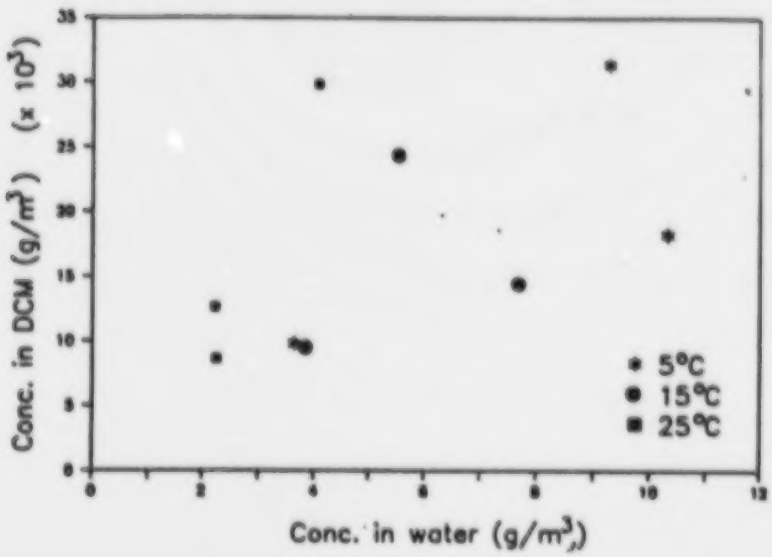


Figure 4.12 Irregularities in the Values of K_{ow} as Illustrated by the Ethylbenzene-DCM-Water System

To assess the operation of the pilot scale column, the equilibrium partition coefficient was measured for toluene and 1,1,2,2-TeCE between Isopar M and water. The K_{ow} was calculated by the two methods mentioned in section 3.2. The maximum difference between the two methods of calculating K_{ow} was 20%. The experiment was conducted three times and agreement between each trial was within 20%. The results of the third trial are summarized in Table 4.3 and Figure 4.13 while the remaining results are presented elsewhere (Adams, 1989).

4.2 Pilot Column Operation

A series of exploratory runs using "spiked" feed was conducted in the summer of 1988. The results from these runs were of little value since the concentration of the solutes in the feed decreased over the duration of the runs. Accordingly, a true steady state was not achieved and an accurate determination of the removal efficiency was not possible. These results are not included in this report. Refinements to the apparatus were made and a second series of experiments was conducted with a modified feed system (as described in section 3.3).

Preliminary runs using pure water as a feed were conducted to determine optimal operating hydraulic parameters for the column. The column was operated at different flowrates and phase ratios while the frequency of agitation was increased until no solvent was visibly entrained in the water outlet stream. The final operating parameters are listed in Table 4.4. The plate spacing was adjusted to create Isopar M droplets of consistent diameter at all points in the column, when water was the continuous phase.

Once the hydraulics were optimized, five runs were conducted using water containing both solutes fed countercurrently to Isopar M. The dispersed phase and the solvent to water (S/W) flow ratios were varied from run to run. For this series of experiments, the amplitude of reciprocation was maintained at 20 mm. The frequency was 65 RPM when Isopar M was the dispersed phase and 150 RPM when the solvent was the continuous phase. Table 4.5 lists the operating conditions for each run. A summary of the results for each run are included in Adams, 1989. These summaries contain a tabulation of the concentration of toluene and TeCE in each phase at specified times, from which the rate of solute removal and the mass balance were calculated (ie. comparing the mass flow of solute in the inlet to that in the outlets). The mass balance agreed to within 7% for TeCE and 20% for toluene except for RUN 3 which had a discrepancy of 40% for toluene and

Table 4.3 Results of the Partition Coefficient Measurement Experiments.

a. TOLUENE

EXT^n #	Concentration in water (g/m^3)	Concentration in Isopar M (g/m^3)	K_{ow}	$-\log(C_w/C_o)$
FEED		5750		
1	7.06	4540	644	0.103
2	5.78	4350	753	0.122
3	6.75	3770	559	0.183
4	4.79	2960	618	0.289
5	ND	2130	—	0.432

$\log(1+V_w/V_oK_{ow})$ = 1.2
V_w = 1 L
V_o = 0.01 L
K_{ow} = 520

b. 1,1,2,2-TeCE

EXT^n #	Concentration in water (g/m^3)	Concentration in Isopar M (g/m^3)	K_{ow}	$-\log(C_w/C_o)$
FEED		27600		
1	88.8	14400	162	0.284
2	54.3	10500	194	0.418
3	39.6	6870	174	0.604
4	23.0	3300	143	0.923
5	ND	1570	—	1.245

$\log(1+V_w/V_oK_{ow})$ = 1.7
V_w = 1 L
V_o = 0.01 L
K_{ow} = 140

ND is not determined, i.e. below detection limit

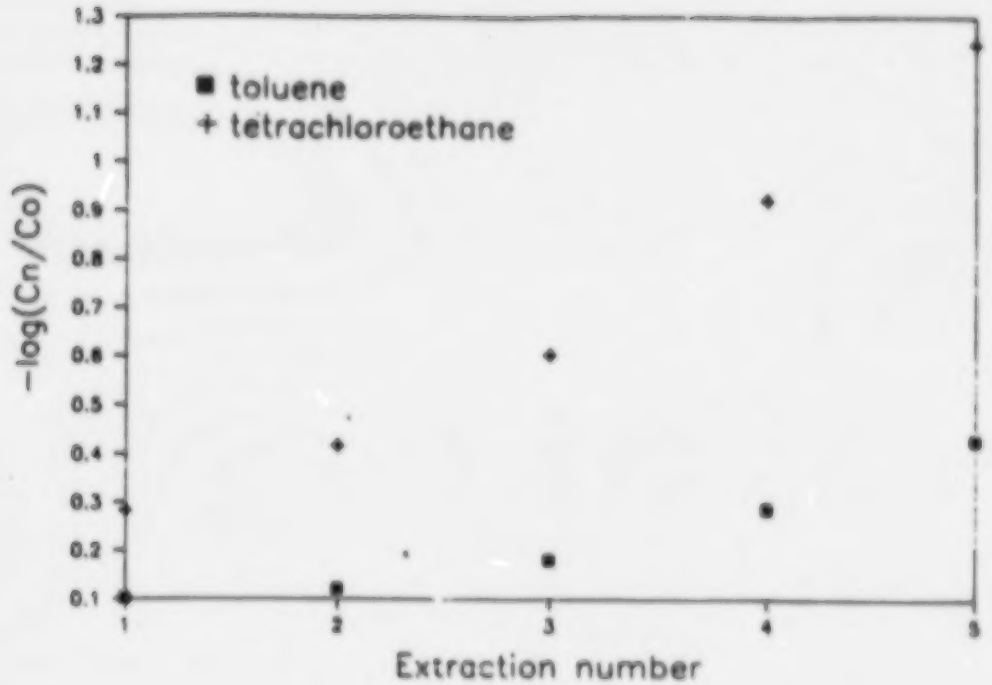


Figure 4.13 K_{oc} Measurement by Sequential Extractions of Isopar M with Water, Third Trial

Table 4.4 Optimal Operating Conditions

a. Isopar M dispersed in water

RUN	AMPLITUDE (mm)	FREQUENCY (RPM)	WATER FLOW (mL/min)	SOLVENT FLOW (mL/min)	S/W
1	20	94	715	16	1/45
2	20	65	1070	100	1/10
3	20	36	1070	50	1/20
4	12.5	12	1070	30	1/30

b. Water dispersed in Isopar M

RUN	AMPLITUDE (mm)	FREQUENCY (RPM)	WATER FLOW (mL/min)	SOLVENT FLOW (mL/min)	S/W
5	12.5	200	360	10	1/35
6	12.5	150	710	15	1/45
7	12.5	150	1070	10	1/100

Table 4.5 Operating Parameters for the Pilot Scale Experiments

RUN	DISPERSED PHASE	S/W RATIO	WATER FLOW (mL/min)	DURATION OF RUN
1	Isopar M	1/10	830	2.7 h
2	water	1/10	830	3.5 h
3	water	1/20	1030	3.0 h
4	water	1/20	750	4.0 h
5	water	1/30	830	4.0 h

33% for TeCE. The rate of solute removal is shown graphically for each run (Figures 4.14-4.18). A milk-like foam formed in the middle of the column during the runs for which water was dispersed in Isopar M. In hindsight it is probable that the column had reached the flooding point (Baird and Shen, 1984).

A sixth run was performed using a semi-batch flow configuration. The Isopar remained stationary in the column while the water was passed through the solvent for a total of 9 hours. The agitation frequency and amplitude used in the previous runs were maintained. The volume of Isopar M in the column was estimated to be 7 L and the water flow was 925 mL/min. The removal efficiencies of this run are shown in Figure 4.19.

Because of the mass balance discrepancies an experiment was designed to estimate the accuracy of the water sampling technique. Repeated samples of water with a known concentration of solute were taken and analysed. The measured concentrations were compared to the known concentrations. The results indicated that the concentration in the water was underestimated by 12% to 40%. The larger discrepancies were with both toluene samples and the higher TeCE concentration. The precision of the injections was within 10% for the two TeCE samples and the higher toluene concentration samples but increased to 15% for the samples with a low toluene concentration. Full results are included elsewhere (Adams, 1989). It is clear that aqueous solutions of toluene and TeCE are very volatile and must be handled carefully to avoid losses.

The results obtained from the pilot scale runs and the determination of the equilibrium line for the two solutes in Isopar M can be used to calculate the number of theoretical stages, N, in the column and the HETS. The accuracy of the water sampling was not taken into account since the HETS equations consider only relative concentrations. A summary of the calculations is given in Table 4.6. The operating line-equilibrium line (McCabe-Thiele) diagram for RUN 4 is shown in Figure 4.20 for toluene and Figure 4.21 for TeCE.

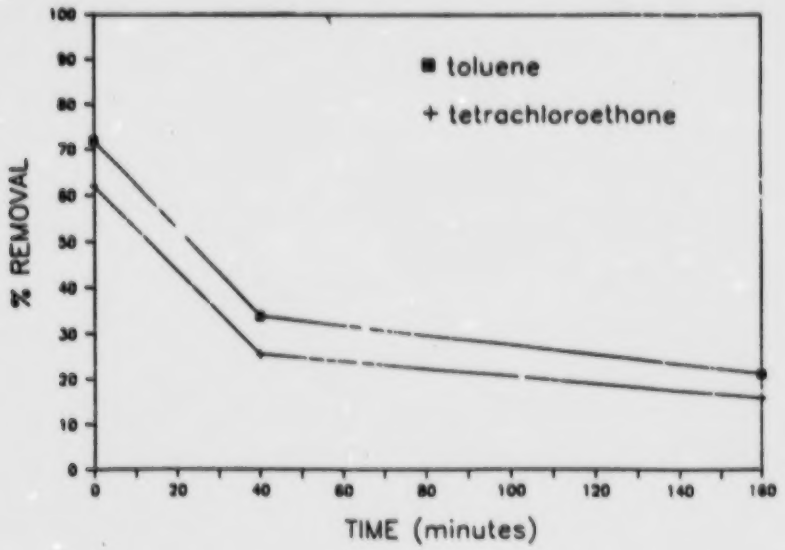


Figure 4.14 Percent of Solute Removal vs. Time for Toluene and TeCE in RUN 1, S/W = 1/10, Isopar M Dispersed in Water

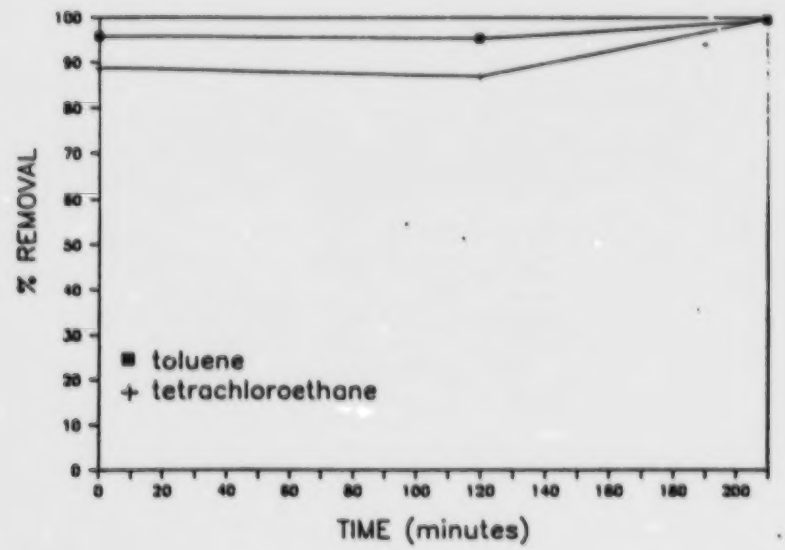


Figure 4.15 Percent of Solute Removal vs. Time for Toluene and TeCE in RUN 2, S/W = 1/10, Water Dispersed in Isopar M

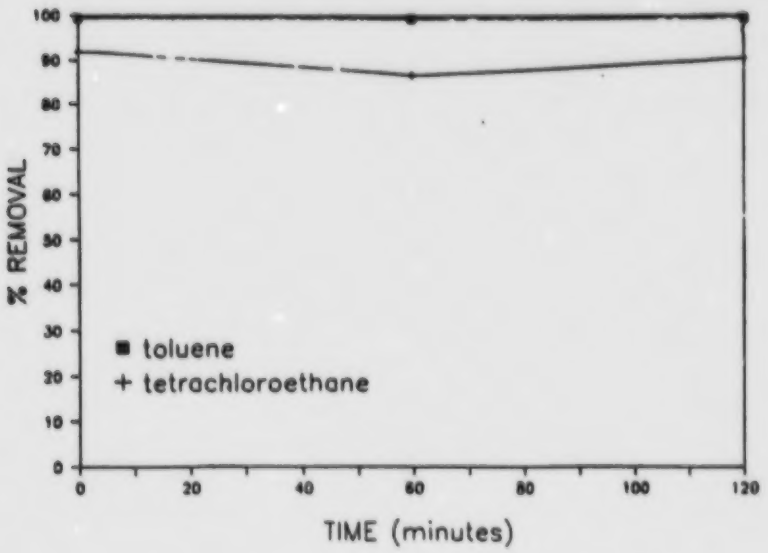


Figure 4.16 Percent of Solute Removal vs. Time for Toluene and TeCE in RUN 3, S/W = 1/20, Water Dispersed in Isopar M

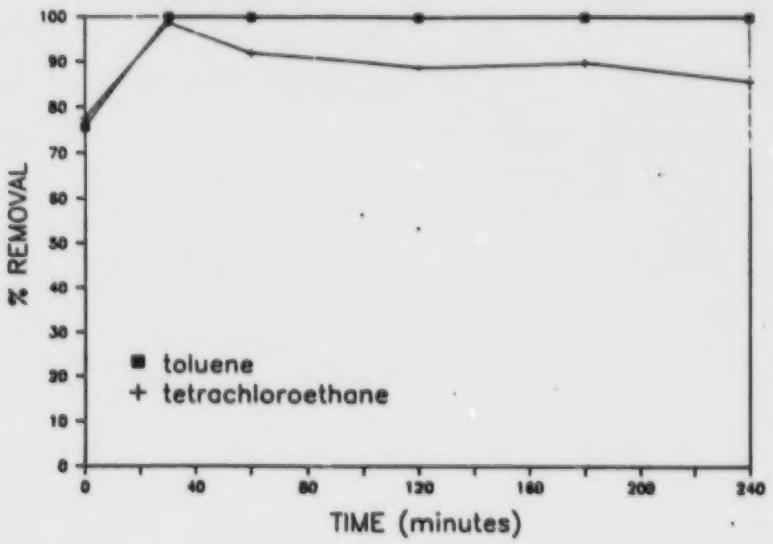


Figure 4.17 Percent of Solute Removal vs. Time for Toluene and TeCE in RUN 4, S/W = 1/20, Water Dispersed in Isopar M

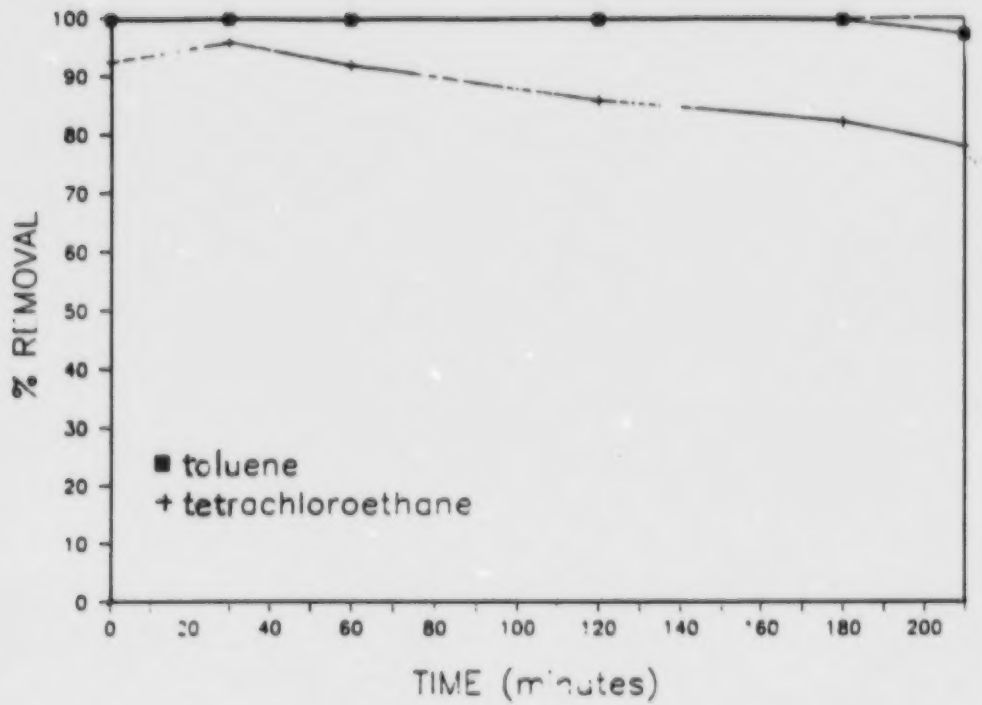


Figure 4.18 Percent of Solute Removal vs. Time for Toluene and TeCE in RUN 5, S/W = 1/30, Water Dispersed in Isopar M

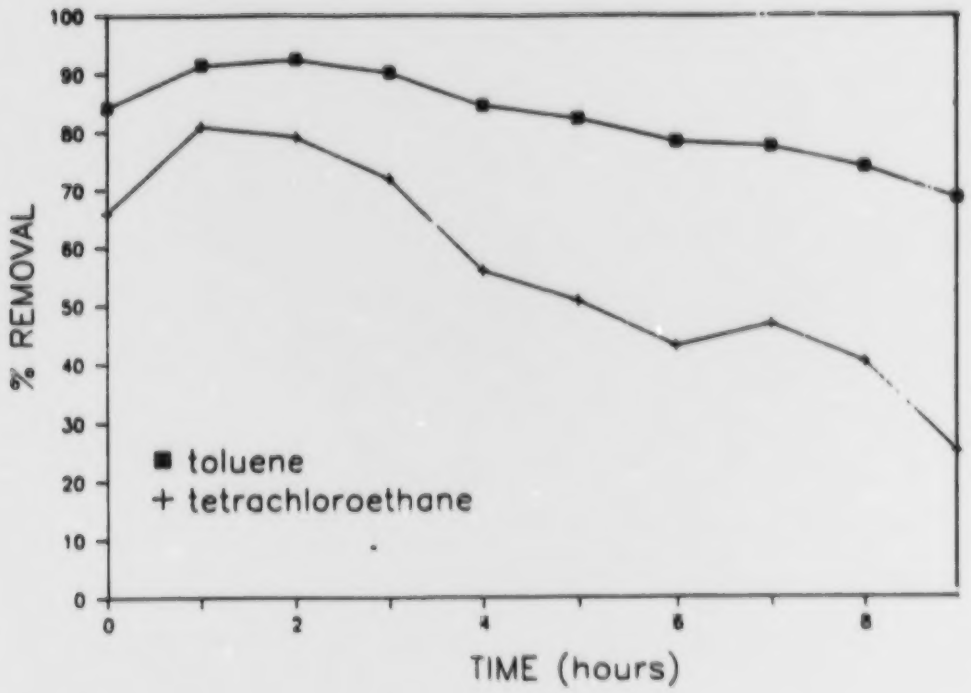


Figure 4.19 Percent of Solute Removal vs. Time for Toluene and TeCE in RUN 6, Semi-batch Operation, Water Dispersed in Isopar M

Table 4.6 Calculation of the HETS for both solutes

a. TOLUENE

Zt = 200 cm
Ys = 0
a (eqn) = 805.8

RUN NO.	Xf	Xr	S'(g/min)	F'(g/min)	a(DL)	e	N	HETS(cm)
1	6.18E-05	4.58E-05	64.9	830	12.78	63.06	0.07	2793.
2	6.62E-05	3.00E-07	70.4	830	11.78	68.44	1.27	157.
3	3.56E-05	2.00E-07	38.4	1030	26.81	30.05	1.51	132.
4	6.97E-05	2.00E-07	26.1	750	28.70	28.08	1.74	114.
5	6.14E-05	2.00E-07	22.1	830	37.43	21.53	1.85	108.

b. 1,1,2,2- TETRACHLOROETHANE

Zt = 200 cm
Ys = 4.80E-04 g/g
a (eqn) = 209.28
Ys/a = 2.29E-06

RUN NO.	Xf	Xr	S'(g/min)	F'(g/min)	a(DL)	e	N	HETS(cm)
1	8.28E-04	6.80E-04	64.9	830	12.78	16.38	0.07	2992.
2	7.00E-04	2.10E-06	70.4	830	11.78	17.77	ERR	ERR
3	3.70E-04	4.47E-05	38.4	1030	26.81	7.80	0.99	201.
4	6.13E-04	8.10E-05	26.1	750	28.70	7.29	0.97	206.
5	4.74E-04	9.86E-05	22.1	830	37.43	5.59	0.83	239.

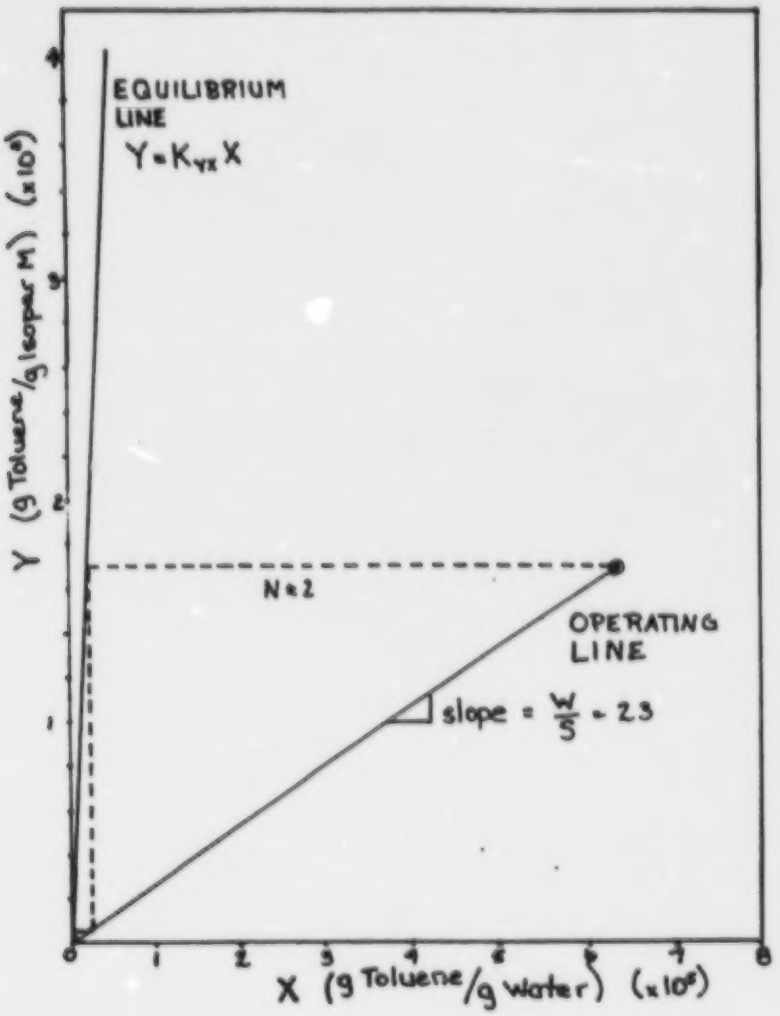


Figure 4.20 McCabe-Thiele Diagram for Toluene in RUN 4

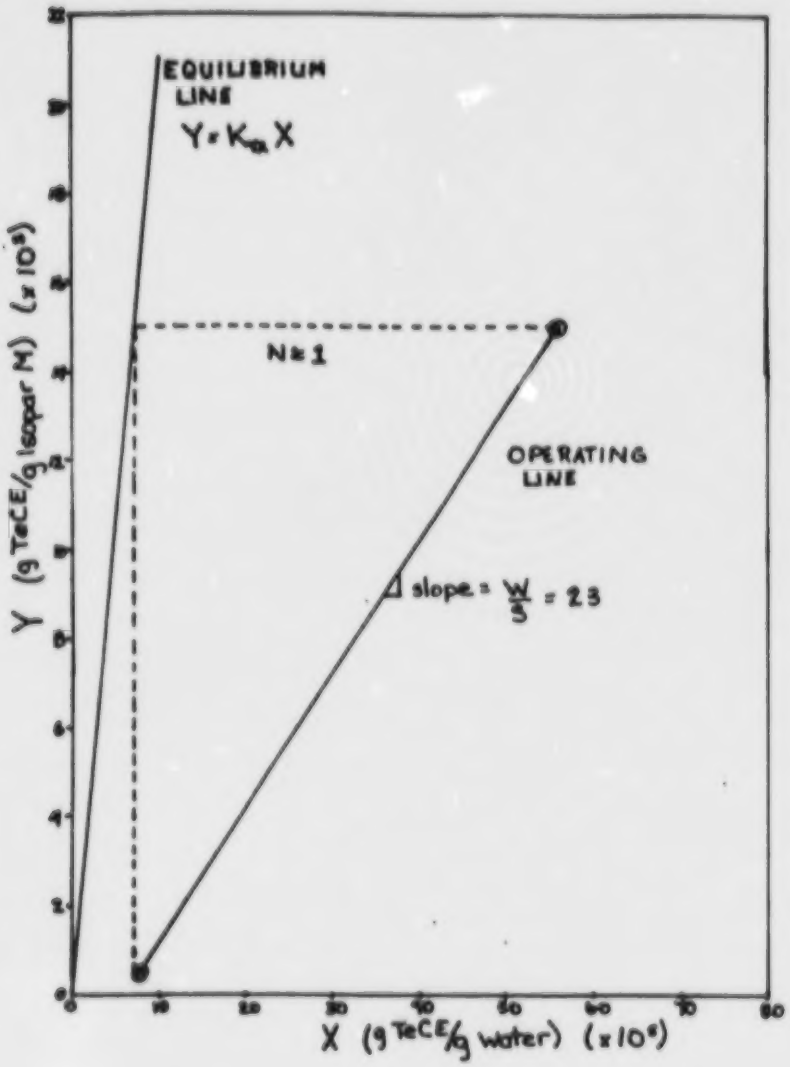


Figure 4.21 McCabe-Thiele Diagram for TeCE in RUN 4

4.3 Steam Stripping

Two runs were conducted in which the extract, consisting of toluene and TeCE dissolved in Isopar M was contacted with steam at different steam flowrates. For the first run the time zero sample contained a water emulsion and did not reflect the true concentration of the solutes in the Isopar M. Therefore the percent removal was calculated from the sample taken at 30 minutes. All of the toluene and 75% of the TeCE was removed in both runs. In the first run the steam flow fluctuated from 9-12 kg/h and the second run had a consistent steam flow of 6.5 kg/h. Approximately 24 kg of steam was used in each run. These volumes are at 1 atmosphere pressure and 100°C. In both cases, the Isopar M was heated to approximately 120°C. The percentage of solute removal for the second run is related to the volume of steam released to the apparatus in Figure 4.22. Tabulated data for the two runs are presented elsewhere (Adams, 1989).

The condensate consisted of an aqueous and an organic phase. The organic phase was determined to be 16% of the total volume of condensate collected. The condensate samples were analysed after the run had concluded. The aqueous phase was analysed for the second run while the organic phase was analysed for both runs. The results (Table 4.7) show high concentrations of the solutes in the organic phase and much lower concentrations in the aqueous phase. The aqueous and organic concentrations were used to calculate the equilibrium partition coefficients. The components of Isopar M which are stripped with the solute act as a solvent with a $K_{_}$ of 660 for toluene and 125 for TeCE.

Comparisons of the chromatograms for the stripped Isopar M, the organic phase of the condensate and the aqueous condensate are given in Figures 4.23 to 4.25. The chromatogram for the stripped Isopar M (Figure 4.23) shows peak areas which are smaller than those of pure Isopar M traces. A small peak (RT: 4.53 minutes) in Figure 4.23 indicates the TeCE is not completely removed but the toluene (RT: 2.9 minutes) is at a concentration below the detection limit.

In Figure 4.24, there are relatively large peaks for toluene (RT: 2.88) and TeCE (RT: 4.58) as well as for the components of the Isopar M with lower boiling points (RT: up to 9 minutes). There are considerably less of the higher boiling compounds in the condensate sample. Figure 4.25 shows that there are detectable but low concentrations of toluene (RT: 2.82) and TeCE (RT: 4.55) in the water phase. The organic phase does not have a detectable solubility in the water as indicated by a lack of peaks after 4.55 minutes.

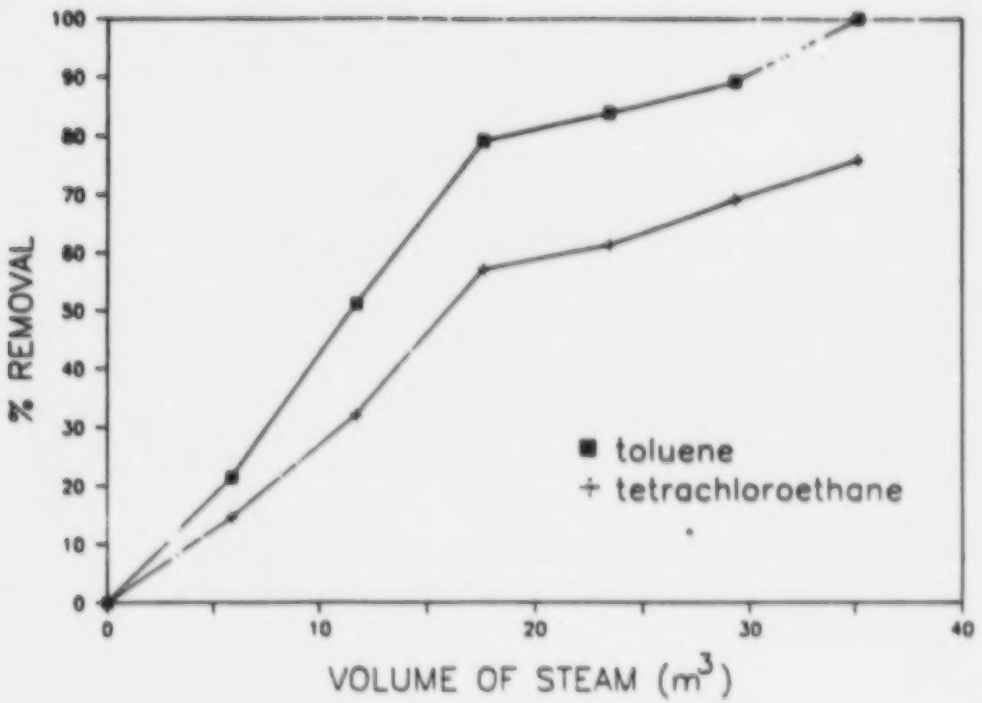


Figure 4.22 Percent of Solute Removal vs. Mass of Steam Added for Toluene and TeCe in RUN 2 of the Steam Stripping Experiments

Table 4.7 Results of the Steam Stripping Experiments

Run	Sample	Concentration of Toluene (g/m^3)	Concentration of TeCE (g/m^3)
1	organic	11600	76500
2	organic	13200	60400
2	aqueous	20	490

Run	Sample	Concentration of Toluene (g/m^3)	Concentration of TeCE (g/m^3)
1	organic	11600	76500
2	organic	13200	60400
2	aqueous	20	490

Figure 4.23 Chromatogram of Isopar M After Steam Stripping for 120 min., TeCe Peak at 4.53 min., Remaining Peaks: Components of Isopar M

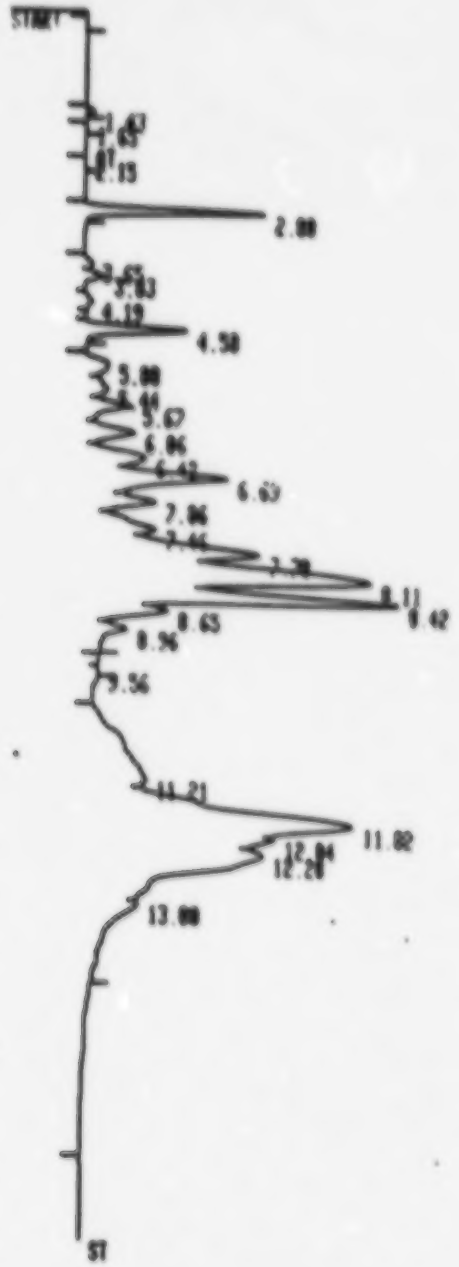


Figure 4.24 Chromatogram of Organic Phase of Steam Condensate, Toluene Peak at 2.88 min., TeCE Peak at 4.53 min., Remaining Peaks: Components of Isopar M

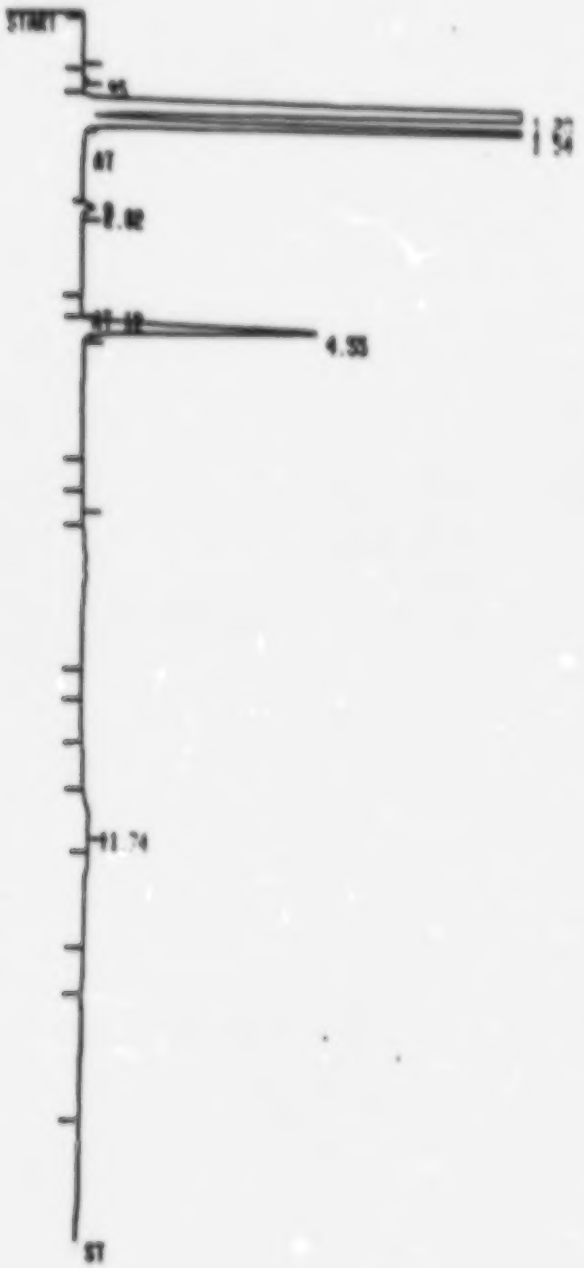


Figure 4.25 Chromatogram of Hexane(RT: 1.28 min.) Extraction of Aqueous Phase of Steam Condensate, Toluene Peak at 2.82 min., TeCE Peak at 4.55 min.

5. Discussion

5.1 Partition Coefficients

Error analysis

The accuracy of the K_{ow} measurements is controlled by errors in sample preparation and errors in analytical technique. The principal source of error for the sample preparation is believed to be fhe inaccurate measurement of the volume of solute introduced to the aqueous and organic phases. The magnitude of the error is indicated by the percent difference in the mass balance for the system. In other words, the amount of solute added, based on the volume of solute, can be compared to the mass of solute as determined f.om the concentration of the solute in the two phases. The discrepancies are not believed to be attributable to volatilization since the deviation is negative (ie. the mass determined from the concentrations is greater than the amount added based on the volume introduced). The solute was introduced to the flask either by pipette or by gas-tight syringe. Neither method is believed to be significantly more accurate than the other. A more accurate method for determining the amount of solute in the samples might have been to weigh the samples before and after the addition of the solute.

The mass balances are not in the ran:ge of 2-3% difference which would be required to determine the K_{ow} by analysis of the solvent phase alone. Despite the substantial deviations from the theoretical mass of the solute (based on volume), the calculated mass (based on concentrations determined by GC analysis) is usually consistent for a given sample at the three temperatures (refer to Table 4.1 for an example). Therefore there is apparently no significant loss of solute over time, and provided the concentration is accurately determined in both phases, the calculated K_{ow} should not be affected.

Two systems, toluene-DCM-water and ethylbenzene-DCM-water, showed a greater lack of consistency for the concentration of the solute in the water phase samples. The toluene samples were initially analysed at 25°C. The analysis shows high water concentrations at 25°C followed by a large drop for all samples at 15°C, remaining at these concentrations for the 5°C analysis. The

concentrations in the solvent phases are not similarly affected. This effect is not believed to be caused by the higher temperature because the same effect is not noticed for any of the other solutes in DCM nor for toluene in any of the other solvents. Nor is it probable that the initial samples were not at equilibrium since Leo, Hansch and Elkins (1977) have shown that equilibrium is established within 1-2 minutes when the sample is repeatedly inverted. The samples in this study were stirred for a minimum of 2 hours and allowed to settle for 8-16 hours. It is more probable that there was some emulsion formation in the water phase. Although undetectable to the eye, the presence of even a small amount of emulsion could cause significant errors in the water concentrations.

The ethylbenzene samples present two problems: a decrease in the water phase concentration over time (from 5°C to 25°C) and a medium concentration which is higher than the high concentration for the water phases at 5°C and 15°C (see Table 5.1, an excerpt from Table B-8, Adams, 1989). Neither of these phenomena are mirrored in the solvent phase. These discrepancies may also be attributed to the presence of undetectable emulsions in the water phase of the samples.

The accuracy of the solute concentration measurement is dependent on the calibration method and the sampling technique. The calibration curves are linear over the range of concentrations considered, with adequate correlation coefficients (greater than 0.9). When the calibration for a single solute was repeated for several solvents, the results were reproducible over a period of several months. Daily calibration checks were also made to ensure that the detection did not drift. On days that significant drift was noted, the areas were adjusted to reflect true concentrations. A significant reduction in the detection is noted for the packed column GC indicating that the FID required cleaning. Since fresh calibrations standards were used, and new calibration lines determined, the accuracy of the measurements should not be affected.

The contamination of the bottom phase by the top phase during sampling is believed to be the principal source of error in the sampling technique. To ensure that the water phases were not contaminated in this way, the solvent peak in the water sample was monitored. For the purge and trap samples using octane and octanol, solutions of water saturated with the solvent were analysed to detemine reasonable solvent peak areas. Since samples did not show contamination for these two solvents, it was assumed the ethylbenzene samples were accurate as well.

Table 5.1 Concentrations of Ethylbenzene in DCM and in Water

Temperature (°C)	Sample	Concentration in DCM (g/m^3)	Concentration in Water (g/m^3)
5°C	1.0 mL	9670	3.6
	1.5 mL	18100	10.3
	2.0 mL	31400	9.3
15°C	1.0 mL	9530	3.9
	1.5 mL	14500	7.7
	2.0 mL	24400	5.5
25°C	1.0 mL	8670	2.3
	1.5 mL	12700	2.2
	2.0 mL	29900	4.1

For the solvent analysis of DCM samples, the solvent peak area was monitored to ensure that it was not below the areas seen during calibration. A low solvent peak area would indicate contamination by water and would result in erroneously low solute concentrations.

Despite knowing the sources of error for the analysis of the aqueous and organic phases, the accuracy of the total analytical process is difficult to quantify. However, a reasonable estimate of the accuracy of the K_{ow} measurement is +/-25%. A measure of the accuracy is possible by comparing the partition coefficients determined in this study to those available in the literature. Literature values are only available for the octanol systems. All three values obtained in this study compare favourably with those reported by other workers (Table 5.2).

Sequential extractions

A measure of the reproducibility of the GC analysis is available from the determination of the K_{ow} of toluene and TeCE between Isopar M and water. The linearity of the relationship between the $-\log(C_w/C_o)$ and the number of extractions (Figure 4.12) indicates the ability of the analytical technique to produce consistent values. This is also seen in the standard deviation (13% for both solutes) for the K_{ow} calculated from the concentrations in both phases. The standard deviation for the areas of a series of injections of the same solution was always within +/-10%.

It is concluded that the method of sequential extractions of the solute from the solvent using water is particularly attractive for the measurement of large values of K_{ow}. The need to analyse the water phase samples with the inherent problems of evaporative losses and emulsion formation is eliminated. The process of contacting a volume of solvent containing solute with repeated volumes of fresh water should result in the significant reduction of the concentration of the solute in the solvent (ie. by a factor of 3 to 10). This enables the rapid and reliable estimation of the K_{ow} using a minimum of analytical effort.

For example, if a water stream is known to be contaminated with a solute and the effectiveness of Isopar M as an extractive solvent is to be tested, the procedure would be to prepare a mixture of say 20 mL of 1% solute in Isopar M. This would be contacted with repeated 1 L volumes of water to remove the solute. The K_{ow} can be estimated by the fractional removal of the solute for each contacting stage, provided the volumes are kept constant. A relatively low fractional removal indicates a favourable solvent.

Table 5.2 Octanol-Water Partition Coefficients

Solute	This Study	Other Studies
1,2-DCE	23	28[a]
1,1,2,2-TeCE	256	245[b]
Toluene	595	537[b]

a. Barbari and King, 1982

b. Hansch, Leo and Elkins, 1971

Magnitude of the partition coefficients

The measured partition coefficients (Table 4.2) are highest for solutes with low solubilities in water. This is particularly apparent for acetone which is miscible in water. 1,2-dichloroethane also has a high solubility in water and a relatively low K_w in each solvent. The relationship between the magnitude of the K_w and the solubility of the solute in water can be expressed graphically (Figure 5.1). The relationship is based on the knowledge that since the K_w is equal to the ratio of the concentrations of the solute in the two phases, it would also be equal to the ratio of the solubility of the solute, S, in the two phases. That is:

$$K_w = C_o/C_w = S_o/S_w \qquad [5\text{-}1]$$

In logarithmic terms, equation [5-1] becomes,

$$\log K_w = \log S_o - \log S_w \qquad [5\text{-}2]$$

Therefore, the plot of log K_w versus log S_w yields straight lines of slope -1 and intercepts of log S_o. Each solvent appears to have one particular value of solute solubility, independent of the solute. Although the number of points for each solvent is limited, the linearity of the relationship is implied in Figure 5.1. Acetone is not included in the plot since its solubility in water is not measurable. The octanol line is supplemented with data from Leo, Hansch and Elkins (1971), for solutes of different solubilities (hexane, styrene, phenol, DCB and ethylbenzene). If a plot as in Figure 5.1 is available for a solvent of interest, the K_w for a solute not included in the plot can be estimated from the value of the solubility of the solute in water. This is tested for the partitioning of benzene between octanol and water. The solubility of benzene is 1780 g/m^3 (Verschueren, 1977) (log 3.25). From Figure 5.1 this translates to a log K_w of 2.5. Leo, Hansch and Elkins, (1971), list the log K_w as 2.13.

Of the solvents considered, DCM appears to be the most effective solvent, followed by ethylbenzene, octanol and octane. This trend is to be expected based on the structures of the four solvents. DCM and ethylbenzene are both relatively compact molecules, hence are not subject to the steric hindrance problems associated with longer and unbranched molecules such as n-octanol and n-octane. All four solvents yield adequate partition coefficients so that based on the K_w they would be suitable (from a partitioning viewpoint) for use on a larger scale.

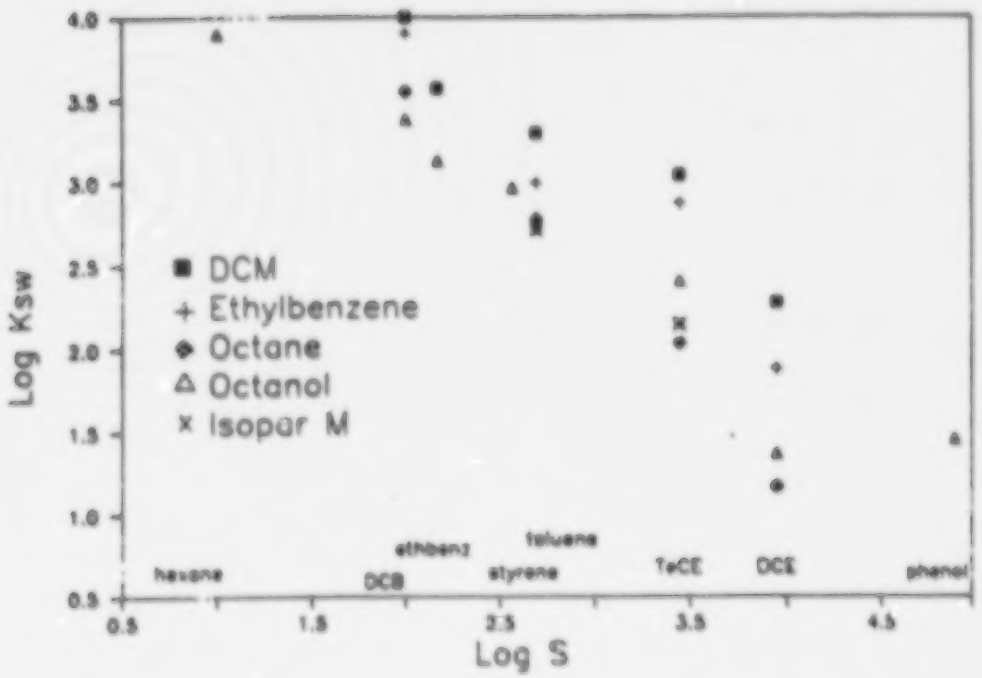


Figure 5.1 Log K_{sw} vs. Log Solubility of a Solute in Water

Effects of temperature on K_w

For the temperature ranges considered, there was no significant effect on the partition coefficients. Gravelle and Panayiotou (1980) report similar results for pure solvents over a wider temperature range (15°C to 60°C). Therefore, a full scale unit would not require temperature control unless it was to be used at sub-zero temperatures.

Summary

Since the objective of this study is to obtain estimates of the partition coefficients rather than precise determinations for thermodynamic purposes, the reasons for the effects noted in the two systems using DCM as a solvent were not pursued. It transpires that the partition coefficients are very large for most of the solutes. More accurate values are not required since the extraction is mass transfer limited rather than equilibrium limited.

5.2 Solvent Selection

In practical applications, the removal efficiency is limited by the mass transfer in the contactor; extremely high values of K_w do not necessarily improve the extraction. In order to obtain high removal efficiencies, the term $K_w S/W$ must be greater than one. However, due to poor hydrodynamic conditions at extreme phase ratios, there is little improvement in extraction efficiencies if $K_w S/W$ is greater than five (Earhart et al., 1977). Modern contacting equipment can operate well at solvent to water flow ratios of 1/20, therefore maximum removal efficiencies will be achieved by solvents with partition coefficients of approximately 100 for the limiting solute (ie. the solute with the lowest K_w). The use of a solvent with a higher K_w implies that excess solvent would be required simply to ensure that the solvent and water phases are well mixed.

Of the solvents considered in this study, octane appears to be the solvent of choice for all solutes except DCE and acetone. Only DCM showed an adequate K_w value for DCE and the removal of acetone from water would be difficult with any solvent. The use of DCM as a solvent for the large scale clean up of contaminated water presents problems due to its high solubility in water. Any water treated with DCM would have to undergo further treatment to remove the solvent. Therefore, dichloromethane is not recommended for use in environmental clean up applications.

Difficulties can arise with the use of octane on a large scale as well due to its high flammability. If similar extraction efficiencies could be obtained by a higher molecular weight hydrocarbon, so that it would still be relatively non-toxic but less flammable, large scale liquid extraction would be safer. The answer to this problem may lie in the use of a hydrocarbon mixture such as kerosene which contains sufficiently low molecular weight compounds for adequate extraction but the molecular weights are sufficiently high to reduce the flammability. By including branched-chain compounds in the solvent mixture, extraction efficiencies may be improved as suggested by Munson and King, (1984). Isopar M contains hydrocarbons ranging from C_{11} to C_{20} with 72% branched-chain compounds. The flash point (a measure of flammability) for Isopar M is 79°C (cc) compared to 13°C (cc) for octane.

The disadvantage to using a mixture of compounds for a solvent is the increased losses during solvent recovery. As noted in the steam stripping process results, the lighter ends of the solvent were stripped along with the solute. This loss must be considered in the design since the effectiveness of the solvent may be reduced with repeated use.

5.3 Pilot Scale Extraction

The preliminary runs investigated the fluid dynamics of the column. The S/W ratios considered (as low as 1/100) were too low for effective mass transfer but the frequency and amplitude of agitation applied at the higher S/W ratios as well. The plate spacing was optimized to give consistent dispersal of the Isopar M in the water. The water phase seemed to be adequately mixed at this spacing so no changes were made when the water was dispersed in the solvent.

The feed concentration did not vary during the runs, indicating that volatilization of the solute from the feed was minimized. Concentrations of both toluene and TeCE did not drop by more than 15% during any run except during RUN 3 in which the initial water concentration dropped by 40% after the first sample. This may be due to an erroneously high first sample.

The accuracy of the water sampling technique is poor, apparently due to volatilization of the solute during sampling. The solute loss could be reduced if the sampling tube were inserted below the layer of hexane in the sampling vial. However, the sample port tubing was too large to insert in the vial. If a disposable glass pipette was attached to the end of the sampling tube, the tip could be placed in the hexane during sampling, and volatilization of the sample would be

eliminated. The pipette could be replaced after each sample to prevent contamination of subsequent samples.

The duration of a run is limited by the size of the feed tank. Runs longer than 4 hours were not possible at low S/W ratios. Since the minimum solvent flow is 30 mL/min the feed would last only 3.5 hours at a S/W ratio of 1/30. In a countercurrent contactor, steady state may be assumed to be approached after 2-3 volumes of the continuous phase have passed through the column. For Isopar M flowing at 30 mL/min, it would take 8-12 hours to approach steady state. At 100 mL/min this time would be reduced to 2.5-3.5 hours. Theoretically, only the first two runs (at S/W of 1/10) could have approached steady state.

The allowable reciprocating frequency was much lower (less than 50%) when Isopar M was dispersed in the water than when the solvent was the continuous phase. This frequency difference may help to explain the results of the first mass transfer run. Based on the high K_{ow} for the two solutes, excellent removal efficiencies should have been possible at a S/W ratio of 1/10. However, at the low frequency the Isopar M, although consistently dispersed in the continuous water phase, was not finely dispersed over the cross-section of the column. As a result, some water could pass through the column (especially near the edges) without contacting with Isopar M. On the other hand, when the solvent is continuous, the full surface area of the water droplet comes in contact with the solvent. In the second case, a greater percentage of the water is in contact with the Isopar M and hence better removal efficiencies are possible. Therefore, in this application, it is concluded that the solvent phase should be continuous and the water phase should be dispersed. An additional advantage of this configuration is that the water feed may be stopped without significantly affecting the condition of the column. This may be of practical advantage when operating under intermittent emergency conditions.

Subsequent runs with the water dispersed in Isopar M showed that high removal efficiencies are possible in a countercurrent contactor. Although true steady state was not achieved in any of the runs, plots show that the steady state assumption is reasonable for RUN 4. The data for RUN 2 shows that removals of 98-99% are possible for both solutes at a S/W ratio of 1/10. In RUN 4 toluene reaches 99% removal but only 85% of the TeCE is removed. The plot for the percent solute removal for RUN 5 implies that a S/W ratio of 1/30 will not allow for sufficient mass transfer for high removal efficiencies with the existing column. Improvements to the column, for example introducing more plates, may increase the mass transfer at lower S/W ratios.

In the semi-batch operation, the amount of solute extracted from the water is not, as expected, as high as in the countercurrent flow configuration. Backmixing effects result in a lower concentration gradient in a semi-batch operation than in a countercurrent flow operation. The percent removal drops quickly for TeCE, the limiting solute, further reducing the appeal of the semi-batch operation. It is concluded that continuous flow operation is preferable but if operating difficulties are encountered, batch or intermitent flow operation is possible, at reduced extraction efficiencies.

The number of theoretical stages obtained graphically from the McCabe-Thiele diagram agree with those determined by equation [2-26]. There are 0.07 theoretical stages for the extraction of both toluene and TeCE when water is the continuous phase. When water is dispersed in Isopar M the number of theoretical stages increases to 1.3-1.8 for toluene and approximately 1 for TeCE. The slope of the operating line for both solutes obtained by the endpoints of the line (ie. the solute concentrations in each stream) agrees with that determined by the ratio of the flowrates. For RUN 4, the operating line has a slope of approximately 20, corresponding to a solvent to water flow ratio of 1/20.

The error indicated in RUN 2 in Table 4.6 (b) may be the result of an inaccurately low concentration of TeCE in the raffinate sample. The concentration of TeCE in the raffinate is less than the term Y_o/K_{xy}, therefore equation [2-26] attempts to take the logarithm of a negative value. By comparison to the number of theoretical stages of the other runs, N should be approximately 1. It is concluded that for the pilot system with TeCE as the limiting solute, one theoretical stage is obtained at a S/W ratio of 1/20. Under these conditions the solute removal efficiency is insensitive to the NTS.

5.4 Steam Stripping Experiments

The steam stripping tests were successful in removing both solutes from the solvent. The 75% removal of the TeCE would not reduce the concentration in the Isopar M stream to a concentration comparable to the initial concentration of the solvent used in the pilot scale experiments. A 95% removal would be required to achieve this, using almost twice the amount of steam. Otherwise, the contaminated Isopar M could be blended with fresh solvent at a ratio of 1:8, contaminated:fresh.

Five percent of the solvent is stripped during the process. Although significant, this loss is small compared to the amount recycled. One benefit of the stripping of the solvent is that the solutes are extracted from the aqueous condensate by the stripped solvent. Therefore the concentration in the water is low enough to be blended with the initial water feed. The actual concentrations in the condensate would depend on the initial solute concentrations in the solvent.

It was estimated that 1500 kg/m^3 Isopar M of steam would be required to reduce the TeCE concentration by 75% and yet only 330 kg/m^3 Isopar M was used. Mass balances for the experiment are reasonable especially since the volume of Isopar M was estimated. The discrepancy between the estimated and the experimental result is believed to be attributable to the nature of the vapour-liquid equilibrium which applies during this contacting. The nature of this equilibrium, ie. the values of the activity coefficient (equation [2-20]) are in some doubt.

The effectiveness of steam stripping for the removal of a solute from the solvent depends on the relative vapour pressures of the solute and the solvent. Isopar M has a vapour pressure of 0.2 kPa. Of the solutes considered in this study, only 1,2-DCB has a lower vapour pressure than 1,1,2,2-TeCE. The low vapour pressure of DCB (0.25 kPa) intimates that this solute would not readily be separated from Isopar M. In this case, and for solutes of similar or lower vapour pressures, recovery of the solvent may not be possible. In these cases, incineration or another destruction method may be required for the extract. The other solutes considered in this study should be effectively stripped from the solute, similarly to TeCE and toluene.

5.4 Miniature Laboratory Test System

It is suspected that Environment Canada may be faced with situations in which it is asked to contribute to the clean up of a specific contaminated water, for example a leachate. Usually a sample of the water will be available. An attractive option would be to devise a small scale, or miniature laboratory bench scale, all glass extraction-stripping system which could be used to test the feasibility of this process sequence. Assuming that 200 litre water samples could be obtained, a convenient system capacity would be about 1 litre with a flow of 0.1 L/min or 6 L/h. Steady state would be reached within one hour permitting various solvents to be tested at a rate of perhaps three per day.

From experience with the miniature and mobile unit performances on identical feeds, scale-up relationships could be developed. An advantage of this approach is that it would permit reliable

assessment of the feasibility of deploying the mobile unit thus avoiding failure as a result of using the system under inappropriate conditions.

6. Design of Full Scale Reciprocating Plate Column

6.1 Sizing

The data from the pilot scale experiments (Table 6.1) is used to calculate the diameter and the height of the full scale column. The diameter of the full scale unit is to be 0.45 m. The HETS would increase to 4.8 m so the total column height would be approximately 5 m. The plate stack would be 4 m high, with 0.5 m available at either end of the column as disengaging sections. By maintaining the relative plate spacing from the pilot scale experiments, 79 plates would be required, 10 plates spaced 2.5 cm apart, 57 plates at 5 cm spacing and 12 plates spaced 7.5 cm apart. Every sixth plate would be a baffle plate to help reduce the effects of backmixing (Karr, 1980). The frequency of agitation would be reduced to 110 RPM and the 20 mm amplitude would be maintained. A summary of the full scale parameters is given in Table 6.2.

Karr (1980) recommends a more detailed pilot scale test program involving determination of the HETS as a function of both the frequency of agitation and the throughput. In this study, the frequency was maintained constant at different throughputs. The results obtained are deemed to be sufficiently accurate for preliminary designs and estimation of the feasibility of LE for the treatment of contaminated water. More extensive pilot scale tests involving 5 to 10 runs are recommended before the design is finalized. In these tests, longer runs would be conducted to ensure steady state was reached, and the frequency would be varied as well as the throughput to better understand how these parameters affect the HETS of the column.

The size of the unit as determined from these experiments is reasonable for a mobile unit. The 5 m column and the plate stack can be segmented into 2 or 3 sections for transportation to the location and easily assembled on-site. Auxiliary equipment such as pumps and a diesel generator would also fit into the truck in a similar fashion to the steam stripper designed by CH2M Hill Engineering (Yau and Giesbrecht, 1989). The capital cost of the equipment is considered in the following section.

Table 6.1 Pilot Scale Data for the Scale Up of the RPC

N (number of theoretical stages)		1
HETS (height equivalent to a theoretical stage):		2 m
Flowrates:		
water:	0.045 m^3/h	
solvent:	0.002 m^3/h	
Total throughput:	0.047 m^3/h	
Column diameter:	0.05 m	
Cross sectional area:	1.96×10^{-3} m^2	
Flow/unit area:	24 m/h	
Frequency of agitation:	150 RPM	
Amplitude of agitation:	20 mm	

Table 6.2 Data for the Full Scale RPC

N (number of theoretical stages):		1
HETS (height equivalent to a theoretical stage):		4.8 m
Flowrates:		
water:	3.0 m^3/h	
solvent:	0.15 m^3/h	
Total throughput:	3.15 m^3/h	
Column diameter:	0.45 m	
Cross sectional area:	0.159 m^2	
Flow/unit area:	20 m/h	
Frequency of agitation:	110 RPM	
Amplitude of agitation:	20 mm	

6.2 Costing

The costing of a stationary chemical plant is based on the cost of manufacturing and installing the major process equipment and estimating costs of piping, instrumentation, buildings, land, auxiliary services, engineering and construction based on factors relating to the cost of the equipment. Inflation is taken into account by Marshall and Swift factors, which are determined quarterly for the chemical process industries. Values of the current M&S factors are available in Chemical Engineering. Several methods, using slightly different factors are available to estimate the contributions of the various components to the total plant cost. The Chilton factors as outlined by Nelson, et al. (1983) are used to cost the unit based on the following assumptions:

1) The major process items are:
   a) an RPC unit of the dimensions indicated in Table 6.2. The unit includes the pulsing mechanism, motor and drive but not the pumps and piping.
   b) two pumps, one for the solvent with a capacity of 0.5 m^3/h and one for the water with a capacity of 3 m^3/h. Centrifugal pumps with metal components are suitable.

2) A steam stripper for solvent processing is available and so is not considered in the cost estimate.

3) The water is pumped to the feed tank and no pretreatment is required.

4) No treatment of the raffinate is required.

The equipment costs for this estimate had a M&S factor of 600, the M&S factor for 1989 is 892.9 (Chemical Engineering). The total cost for a mobile RPC unit is estimated to be approximately $194,000 in 1989 Canadian dollars. This estimate is accurate to +/-30%. The summary of the estimate with appropriate comments is given in Table 6.3.

Table 6.3 Costing of the Full Scale RPC

	ITEM	COST, $	COMMENTS
1.	FOB equipment	28,000	Woods, 1983, M&S=600
2.	Freight, tax and duties	2,800	0.1 of 1
3.	Subtotal, delivered	30,800	
4.	Installation	15,400	0.5 of 3
5.	Installed cost	46,200	total 3+4
6.	Process piping	13,860	0.3 of 5
7.	Instrumentation	920	0.02 of 5, very little
8.	Auxiliaries (power, steam, water)	460	0.01 of 5, minor item
9.	Buildings, site development, outside lines	0	mobile unit
10.	Total physical plant costs		61,440
11.	Engineering and construction	15,360	0.25 of 10, simple
12.	Contingency and contractors fees	15,360	0.25 of 10, process subject to change
13.	Size factor	18,430	0.3 of 10, small experimental unit.
14.	Total unit cost	110,590 $US	
15.	Conversion to 1989 Canadian dollars	193,600	M&S=892.9, 0.85x$CDN=$US

Since the operating costs will vary depending on unknown variables such as the location of the spill, the type of contaminant and the required solvent, no attempt is made to estimate operating costs. Provided the solvent can be recycled, the costs are expected to be similar to other spill clean up units. The labour and maintenance requirements of the RPC are low.

7. Conclusions

7.1 Partition Coefficient Measurements

1. The K_w was determined for six solutes in one or more of four solvents. The accuracy of the values obtained is estimated to be within +/-25%. Principal sources of error include inaccurate measurement of the solute added to the samples and the presence of undetectable emulsions in the water phases of some samples.

2. The four solvents investigated give high K_w values for most of the solutes. DCM consistently has higher K_w values than the other three solvents, despite its high solubility in the water phase. Octane and octanol have the lowest values of K_w but values are still high except for acetone and dichloroethane. These two solutes have relatively high solubilities in water and are not readily extracted from an aqueous solution.

3. Acetone has such a low K_w in octane that the partitioning was not considered for the other solvents. The K_w of 0.07 is so low that very large solvent to water flow ratios would be required to achieve reasonable extraction efficiencies. Therefore LE is not an ideal process for the removal of acetone from water.

4. DCE may be difficult to remove from water due to its high solubility in water and relatively low K_w for most of the solvents. A solvent such as DCM would effectively remove DCE from water at S/W ratios of 1/20. A solvent similar to octane would require a higher S/W ratio, for example 1/5.

5. The method of sequential extraction developed in this study is a rapid and sufficiently accurate method for the estimation of K_w. Analysis of the water phase, with its inherent difficulties, is not required for the accurate estimation of K_w using this method.

6. The relationship between log K_w and the logarithm of the solubility of the solute in water provides a convienient screening method for estimating the K_w of a solvent for a solute,

provided that the K_w of that solvent for several other solutes is available. The plot of log K_w versus log S_o, yields a straight line of slope -1.

7.2 Pilot Scale Experiments

1. Removal efficiencies of 99% for toluene and 85% for 1,1,2,2-TeCE are obtained at a S/W ratio of 1/20, with the water dispersed in the Isopar M, at a frequency of agitation of 150 RPM. At these conditions the column is operating with one theoretical stage for the limiting solute, TeCE.

2. The extraction efficiency is higher when the water phase is dispersed in a continuous Isopar M phase. This is attributed to better mass transfer conditions when the extracting phase is continuous.

3. Continuous countercurrent flow was more efficient than semi-batch operation. The decrease in efficiency is attributed to a lower concentration gradient in the semi-batch process. The removal for the semi-batch operation decreased after 3-4 hours of operation. Initial removal efficiencies were 90% for toluene and 80% for TeCE.

4. The estimated value of the HETS for the extraction of TeCE is 2 m, indicating that the column has one theoretical stage. The graphical results from a McCabe-Thiele diagram agree with those determined by the Kremser equation.

5. A full scale RPC designed to treat 3 m^3/h of water would be 5 m high and 0.45 m in diameter. The plate stack would be 4 m high with 79 plates. The estimated cost of the unit is approximately $194,000 in 1989 Canadian dollars.

7.3 Steam Stripping Experiments

1. Steam stripping effectively removed the two test solutes from the Isopar M. However, solutes with relatively low vapour pressures (ie. similar to that of Isopar M) may not be adequately removed from the solvent. For these solutes, an alternative method of solvent recovery or solvent destruction would be required.

2. A portion of the solvent is stripped along with the solutes. This may inhibit the performance of the solvent after repeated use. An advantage to the co-stripping of solvent is that the solute concentration in the aqueous condensate is quite low since the organic phase acts as an extractant for the solutes in the water.

3. The estimation method for the prediction of the volume of steam was approximately 5 times higher than the experimental result. More accurate values for the activity coefficients of the solute in the solvent would improve the estimation.

8. Recommendations

1. The data base for partition coefficients should be expanded to include more of the compounds on Environment Canada's list of frequently spilled chemicals. Solvents available on the Canadian market should be investigated. Consideration should be given to the chemical structure of both the solvent and the solutes, and properties such as the vapour pressure and the boiling point of both the solvent and the solute. These properties will affect the attainable extraction efficiencies and the solvent recovery process.

2. Further pilot scale experiments should be conducted to establish the relationship between the HETS and the frequency of agitation. These tests would allow for the most efficient use of the full scale unit by better defining the column parameters.

3. Further testing of the solvent, after steam stripping, is recommended to determine the effects of the deterioration of the solvent. The life expectency of the solvent should be determined to properly assess the operating costs of the unit.

4. Consideration should be given to developing a miniature bench-top all glass simulator of the mobile liquid extraction system.

Nomenclature

Variables

a	activity
C	concentration of the solute, g/m³
d	diameter of the column, m
e	extraction factor
f	fugacity, Pa
f	frequency of agitation, RPM
F_s	steam flowrate, m³/h
HETS	height equivalent to a theoretical stage, m
K_{ow}	partition coefficient of the solute between the solvent and water
k_{ow}	partition coefficient on a molar basis
K_s	steam stripping constant
K_{YX}	partition coefficient based on mass fractions
MW	molecular weight, g/mol
N	number of theoretical stages
P°	vapour pressure, Pa
P_i	partial pressure, Pa
R	Universal gas constant, 8.314 Pam³/molK
S	solvent flowrate, m³/h, or solubility of solute, g/m³
t	time, h
T	absolute temperature, K
v	molar volume, m³/mol
V	volume, m³
W	water flowrate, m³/h
x	mole fraction of solute, mol solute/mol solvent
X	mass fraction of solute in water, g/g
Y	mass fraction of solute in solvent, g/g
Z	height of the column, m

Greek Characters

γ	activity coefficient of solute
ρ	density, kg/m^3

Superscripts and Subscripts

e	extract stream
f	feed stream
i	phase of interest
n	total number of extraction stages or power indicating difficulty of an extraction
r	raffinate stream
s	solvent
v	vapour stream
w	water

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